

Stabilization and Solidification of Nitric Acid Effluent Waste at Y-12

Energy Systems Division

About Argonne National Laboratory

Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY

Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via DOE's SciTech Connect (<http://www.osti.gov/scitech/>)

Reports not in digital format may be purchased by the public from the National Technical Information Service (NTIS):

U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandria, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703)
605-6000 Fax: (703) 605-6900
Email: orders@ntis.gov

Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: reports@osti.gov

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

Stabilization and Solidification of Nitric Acid Effluent Waste at Y-12

by
Dileep Singh and Cinta Lorenzo-Martin
Energy Systems Division, Argonne National Laboratory

December 2016

ACKNOWLEDGMENTS

The work at Argonne National Laboratory was supported by Consolidated Nuclear Security, LLC via Memorandum Purchase Order 4300097546. Helpful discussions with Ms. Alice Lay of CNS Y-12 facility are much appreciated.

(Blank Page)

CONTENTS

ACKNOWLEDGMENTS	iii
ABBREVIATIONS	x
EXECUTIVE SUMMARY	1
1 INTRODUCTION	2
2 CERAMICRETE PHOSPHATE-BONDED CERAMIC	3
3 SAMPLE PREPARATION	4
3.1 Waste Simulant Formulation	4
3.2 Ceramicrete Raw Materials	4
3.3 Waste Form Fabrication	6
3.3.1 Waste Forms for Physical Characterizations	6
3.3.2 Waste Forms for TCLP and ANS 16.1 Test	8
4 PHYSICAL PROPERTY CHARACTERIZATIONS	9
4.1 Expansion Evaluation	9
4.2 Density	10
4.3 Compressive Strength of As-fabricated Samples	10
4.4 Summary	12
5 WATER IMMERSION TEST	13
5.1 Waste Form Appearance	13
5.2 Weight Loss Measurements	13
5.3 Compression Strength	23
5.4 Water Immersion Testing of Waste Forms Fabricated Using Cerium Sulfate as Surrogate	24
5.5 Summary	28
6 AMERICAN NUCLEAR SOCIETY'S 16.1 LEACHING TEST	29
6.1 Leachability Index Determination	29
6.2 Analysis of Waste Forms after ANS 16.1 Test	31
6.3 Summary	33
7 TOXICITY CHARACTERISTIC LEACHING PROCEDURE	34
7.1 Analysis of Hazardous Contaminants in the Waste Simulants	34
7.2 Summary	36
8 CONCLUSIONS	37
9 RECOMMENDATIONS	38
REFERENCES	39

CONTENTS (Cont.)

Appendix A: Compressive Strength Data	40
A.1 As-fabricated Waste Forms.....	40
A.2 Post Water Immersion Test.....	40
Appendix B: AVERAGE Weight Loss Data.....	41
Appendix C: Diffusivities of Selected Ceramicrete Waste Forms as Obtained from ANS 16.1 Test	42
Appendix D: TCLP DATA	46

FIGURES

2-1	Schematic of Ceramicrete process.....	3
3-1	As-prepared baseline waste simulant with cerium in form of cerium oxide	5
3-2	As-prepared baseline waste simulant with cerium in form of cerium sulfate	5
3-3	Slurry of Ceramicrete mix with Class C fly ash and waste simulant	7
3-4	Ceramicrete waste form for CaSiO_3 filler and 20 wt.% waste simulant	7
3-5	Waste simulant stock solution containing RCRA metals 100X the target value of the actual waste.....	8
4-1	As-fabricated waste form for ~30 wt.% Class C fly ash and 25 wt.% waste simulant	9
4-2	As-fabricated waste form for ~30 wt.% CaSiO_3 and 20 wt.% waste simulant	9
4-3	Test setup on Instron for measurement of waste form compressive strength	11
4-4	Compressive strength of waste forms with baseline waste simulant having fly ash and CaSiO_3 fillers.....	12
5-1	Waste form samples with 15 wt.% waste simulant loading and fly ash filler:(a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing	14
5-2	Waste form samples with 20 wt.% waste simulant loading and fly ash filler: (a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing	15
5-3	Waste form samples with 25 wt.% waste simulant loading and fly ash filler: (a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing.	16
5-4	Waste form samples with 15 wt.% waste simulant loading and CaSiO_3 filler: (a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing	17
5-5	Waste form samples with 20 wt.% waste simulant loading and CaSiO_3 filler: (a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing	18

FIGURES(Cont.)

5-6	Waste form samples with 25 wt.% waste simulant loading and CaSiO_3 filler: (a) as- fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing	19
5-7	Weight loss of waste forms during 30-day water immersion for fly ash filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings.....	20
5-8	Weight loss of waste forms during 60-day water immersion for fly ash filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings.....	20
5-11	Weight loss of waste forms during 60-day water immersion for CaSiO_3 filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings.....	22
5-12	Weight loss of waste forms during 90-day water immersion for CaSiO_3 filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings.....	22
5-13	Compressive strength of waste forms with various waste loadings and fly ash filler as a function of immersion time	23
5-14	Compressive strength of waste forms with various waste loadings and CaSiO_3 filler as a function of immersion time	24
5-15	Waste form samples with 20 wt.% waste simulant loading and fly ash filler: (a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing. Cerium in form of cerium sulfate was used as surrogate for uranium.....	25
5-16	Waste form samples with 20 wt.% waste simulant loading and CaSiO_3 filler: (a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing. Cerium in form of cerium sulfate was used as surrogate for uranium.....	26
5-17	Weight loss of waste forms during 90-day water immersion for fly ash and CaSiO_3 fillers with 20 wt.% waste loading	27
6-1	Samples with 20 wt.% waste loading and fly ash filler after 90-day ANS 16.1 test....	31
6-2	Samples with 25 wt.% waste loading and fly ash filler after 90-day ANS 16.1 test....	31
6-3	Samples with 20 wt.% waste loading and CaSiO_3 filler after 90-day ANS 16.1 test ..	32
6-4	Samples with 25 wt.% waste loading and CaSiO_3 filler after 90-day ANS 16.1 test ..	32

TABLES

3-1	Waste form compositions (wt.%) with waste simulant with cerium oxide	7
3-2	Waste form compositions (wt.%) with waste simulant with cerium sulfate	7
4-1	Density of waste forms fabricated using baseline waste simulant	10
6-1	Average leachability indices of key elements from ANS 16.1 tests conducted on various waste forms	30
6-2	Average leachability indices of RCRA metals from ANS 16.1 tests conducted on various waste forms	30
7-1	Hazardous metal and Ce concentrations targeted in waste simulant.....	34
7-2	Hazardous metal concentrations in the in-house-prepared waste simulant.....	35
7-3	Hazardous metal concentrations in the fly ash used for fabrication of the waste forms	35
7-4	Hazardous metal concentrations (ppm) in the fabricated waste forms.....	36
7-5	TCLP results on various waste forms (mg/L)	36

ABBREVIATIONS

ANS	American Nuclear Society
CNS	Consolidated Nuclear Facility
DOE	Department of Energy
ICP-MS	Induction Coupled Plasma–Mass Spectroscopy
LI	Leachability Index
RCRA	Resource Conservation and Recovery Act
SEM	Scanning Electron Microscopy
TCLP	Toxicity Characteristic Leaching Procedure
UTS	Universal Treatment Standard

EXECUTIVE SUMMARY

Consolidated Nuclear Security, LLC (CNS) at the Y-12 plant is investigating approaches for the treatment (stabilization and solidification) of a nitric acid waste effluent that contains uranium. Because the pH of the waste stream is 1-2, it is a difficult waste stream to treat and stabilize by a standard cement-based process. Alternative waste forms are being considered. In this regard, Ceramicrete technology, developed at Argonne National Laboratory, is being explored as an option to solidify and stabilize the nitric acid effluent wastes.

The Ceramicrete process has been demonstrated on a nitric acid waste formulation provided by CNS. The waste simulants were prepared in-house. Waste forms were fabricated with two filler materials: Class C fly ash and CaSiO_3 . Optimum waste loadings as high as 25 wt.% were investigated.

Waste forms for physical characterizations were fabricated with a radionuclide surrogate (cerium) for uranium. Physical property characterizations (density, compressive strength, and 90-day water immersion test) showed that the waste forms were stable and durable. Compressive strengths were >2,000 psi, and the strengths remained high after a 90-day water immersion test. Waste form weight loss was ~2-3 wt.% over the 90-day immersion test. The majority of the weight loss occurred during the initial phase of the immersion test, indicative of washing off of residual unreacted binder components from the waste form surface.

Waste forms for ANS 16.1 leach testing contained appropriate amounts of cerium as the uranium surrogate, along with the hazardous contaminants according to the Resource Conservation and Recovery Act (RCRA). The leachability index for Ce was found to be extremely high (>25) for all the samples evaluated. The higher the leachability index, the better is the waste form in containing the element. Typically, a leachability index of 6 and above is considered acceptable. Further, leaching indices of waste form matrix elements such as Mg, Ca, Si, and P were > 17, indicative of the structural integrity of the waste forms over the 90-day leaching test. Leaching test results were similar for both the 20 wt.% and 25 wt.% waste loadings.

Results from the toxicity characteristic leaching procedure (TCLP) showed that all the hazardous contaminants were contained in the waste, and the hazardous metal concentrations were below the Universal Treatment Standard (UTS) limits.

Flexibility in treating waste streams with wide-ranging compositional make-ups and ease of process scale-up are attractive attributes of Ceramicrete technology.

1 INTRODUCTION

The U.S. Department of Energy's CNS facility at the Y-12 plant in Oak Ridge, TN, is seeking various approaches to treat and stabilize nitric acid waste effluent. This waste effluent is generated from other in-house processes. The nitric acid waste effluent contains uranium as the key radionuclide. In addition, it has various RCRA hazardous metals. The key hazardous and radioactive elements in the waste stream are As (<35 ppm), Ba (<650 ppm), Cd (<330 ppm), Cr (<1000 ppm), Pb (<125 ppm), Hg (<10 ppm), Se (<75 ppm), Ag (<15 ppm), and U (<60,000 ppm). The pH of the waste is highly acidic (<1). Since this is a difficult waste stream to treat, CNS is seeking technologies for stabilization and containment of the waste stream in a robust waste form.

Ceramicrete, a low-temperature forming phosphate ceramic, was developed at Argonne National Laboratory as part of DOE's Environmental Management program to stabilize and contain radioactive and hazardous contaminants (such as Tc, Cs, and Hg) that can volatilize during a high-temperature immobilization process. In previous work, Ceramicrete technology has been demonstrated on various waste streams (liquids, fly ashes, and debris) and has been shown to successfully contain both radioactive (U, Tc, Pu) and hazardous contaminants (Hg, Pb, Cr, etc.) [1-6]. Because of the robustness of the Ceramicrete technology in handling waste streams with varying chemical compositions and pH values, it is a logical technology for treatment of the nitric acid effluents.

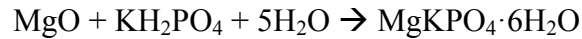
The specific objectives of this laboratory-scale work were three-fold:

- (a) develop and optimize Ceramicrete binder formulations to stabilize and encapsulate nitric acid effluent waste simulant,
- (b) conduct physical characterizations on the waste forms, and
- (c) evaluate the waste forms for leaching of the contaminants.

As a result of this study, waste form compositions, loadings, and performances have been optimized. Results from this study will form the basis of an engineering-scale demonstration on stabilization of secondary waste streams using Ceramicrete technology.

2 CERAMICRETE PHOSPHATE-BONDED CERAMIC

Ceramicrete is fabricated by acid/base reaction of magnesium oxide and mono-potassium phosphate, which when mixed with water form a slurry that sets into a hard ceramic in a few hours. The process is simple and quite similar to the Portland cement process and easily scalable, as shown schematically in Fig. 2-1. No additional equipment requirements are needed. Ceramicrete is a strong (as high as 10,000 psi compressive strength) but dense matrix, and has superior ability to bind contaminants, making it an excellent candidate for microencapsulation. The chemical reaction for Ceramicrete formation can be represented as [1-3]:



The resulting $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ phase is extremely stable and has a solubility product of 2×10^{-11} under ambient conditions. There is no residual water in the system; it is bound as the water of hydration. Ceramicrete has a unique property of binding to itself, unlike cement concrete. Thus, Ceramicrete is easy to repair or patch.

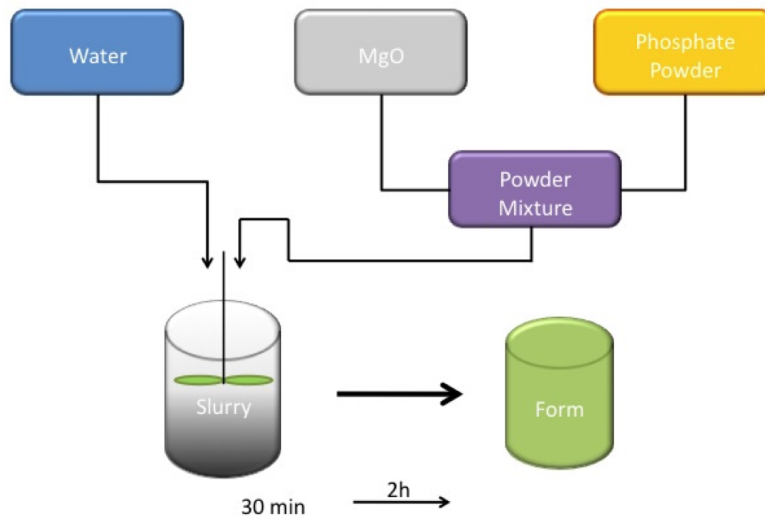


Figure 2-1. Schematic of Ceramicrete process

Because of the flexibility of this process, various second-phase materials may be added for higher strength, fracture toughness, and reduced porosity. For example, one can add as much as 80 wt.% fly ash to Ceramicrete dry powder mix. There is no specific requirement of the particle size of the fly ash. In addition to the phosphate bonding, silicon-phosphate bonding that provides enhanced structural properties may also occur in Ceramicrete [2].

3 SAMPLE PREPARATION

3.1 Waste Simulant Formulation

The waste simulant for initial scoping tests was prepared per CNS's guidance. First, a solution of 0.01 M nitric acid waste was prepared. The batch prepared was 4 L. The pH of the prepared solution was <1. To simulate uranium, cerium was used in the form of cerium oxide. The loading of cerium in the waste stream was 60,000 ppm. The mixture was stirred for several hours with a stir bar on a stir plate. The density of the fabricated solution was 1.08 g/cc. Figure 3-1 shows the fabricated nitric acid solution loaded with cerium oxide. For the initial scoping tests, no RCRA metals were used. It should be noted that "water stream" and "waste simulant" are used interchangeably throughout the text.

In addition to the waste simulant with cerium oxide, another batch was prepared with a more soluble cerium compound, cerium sulfate. The reason for this choice was that cerium oxide, over time, settles out from the liquid phase because of its limited solubility in the nitric acid solution. To avoid this issue, we decided to use cerium sulfate for cerium additions to the waste solution. Nevertheless, thorough mixing of the simulant was done before using it to prepare the waste forms.

We prepared a batch of one-liter size of the waste stream with cerium sulfate. Figure 3-2 shows the fabricated waste effluent using cerium sulfate. This waste stream for initial scoping tests was prepared per CNS's guidance. First, we prepared a solution of 0.01 M nitric acid waste. The pH of the prepared solution was approximately 0.80. The loading of cerium in the waste stream was 60,000 ppm. The density of the fabricated solution was 1.1 g/cc. No RCRA metals were used for the time being. On discussions with CNS, we decided not to pursue the cerium sulfate option; hence, the samples were made but were not characterized in any detail.

The waste simulant was prepared in-house with analytical grade chemicals procured from commercial suppliers. Formulations were prepared for the waste simulant with and without RCRA metals. The waste simulants without RCRA metals were used in various scoping tests such as density, compressive strength, and water immersion test. Waste streams with RCRA metals were used in fabricating waste forms that underwent the leach tests such as the Toxicity Characteristic Leaching Procedure (TCLP) [7] and American Nuclear Society (ANS) 16.1 procedure [8].

3.2 Ceramicrete Raw Materials

Base ingredients to produce Ceramicrete are magnesium oxide, potassium phosphate (MKP), boric acid, and water. In addition to these, a filler material is added. Two types of fillers were used in the study: Class C fly ash (LaFarge) and calcium silicate (wollastonite, Nyco). Further, small amounts of reducing agent, such as potassium sulfide, were added as needed for stabilization of mercury.



Figure 3-1. As-prepared baseline waste simulant with cerium in form of cerium oxide



Figure 3-2. As-prepared baseline waste simulant with cerium in form of cerium sulfate

3.3 Waste Form Fabrication

3.3.1 Waste Forms for Physical Characterizations

Waste forms were fabricated by first placing the requisite amount of base binder ingredients in a bowl and mixing for 5 min. Then, depending on the amount of waste loading targeted, waste simulant was added to the dry powder. In some cases, water was added to produce a slurry with uniform consistency. The mixture was typically stirred for 25-30 min to produce a slurry (Fig. 3-3). This slurry was poured into plastic syringe molds (0.5-in. diameter by 4 in. long) for curing (Fig. 3-4). Samples were left for curing for at least 2 weeks before extracting them from the molds for evaluation. The optimum time for full cure of the waste form was not determined as part of this study. Laboratory-scale waste forms were fabricated at batch size of ~200-250 cm³. For the waste forms fabricated for physical characterization, RCRA metals were skipped in the waste simulants.

Tables 3-1 and 3-2 show the composition of the various waste forms fabricated with cerium oxide and cerium sulfate as the source of radionuclide surrogate, respectively. Waste loading is presented in weight percent (wt. %) and is defined as on the basis of additions made in preparing the slurry:

$$\frac{(\text{weight of waste simulant})}{(\text{weight of waste simulant} + \text{weight of all other ingredients})} \times 100$$

For fly ash as a filler and CaSiO₃ filler, waste loadings were 20 wt.% and 25 wt.%. In addition, in the beginning of the project, some samples were fabricated with 15 wt.% loading as well. The total amount of waste simulant and water added was approximately constant. Any additional water added was qualitative and based on achieving the desired consistency of the slurry.

The nomenclature followed in naming the various formulations in Tables 3-1 and 3-2 is in terms of the filler (where FA is fly ash, and CaSi is CaSiO₃) and waste loading (W). The number represents the waste loading in weight percent on a wet basis. For example, “20W-FA” translates to 20 wt.% waste simulant on a wet basis with fly ash as the filler. The data in the tables show the nominal compositions of the fabricated forms..

During the fabrication of the waste form samples, the goal was to mix the slurry for approximately 30 min. During the mixing sequence, the temperature and pH of the slurry were also monitored. The typical temperature rise of the slurry over 30 min of mixing was 40°C for the 200-250 cc batches, and the pH of the slurry was 5.5-6.40.



Figure 3-3. Slurry of Ceramicrete mix with Class C fly ash and waste simulant



Figure 3-4. Ceramicrete waste form for CaSiO_3 filler and 20 wt.% waste simulant

Table 3-1. Waste form compositions (wt.%) with waste simulant with cerium oxide

	MgO	MKP	Waste Stream	Fly Ash	CaSiO_3	Boric Acid	Water
15W-FA	10.3	34.7	15	31.6		0.35	8.5
20W-FA	10.4	34.8	19.9	31.3		0.35	3.3
25W-FA	10.4	35	24.7	29.7		0.33	0
15W-CaSi	10.3	34.7	15		31.2	0.35	8.5
20W-CaSi	10.3	34.7	19.8		31.2	0.35	3.7
25W-CaSi	10.4	34.9	24.7		29.6	0.33	0

Table 3-2. Waste form compositions (wt.%) with waste simulant with cerium sulfate

	MgO	MKP	Waste Stream	Fly Ash	CaSiO_3	Boric Acid	Water
20W-FA	10.3	34.7	19.5	31.2		0.35	3.7
20W-CaSi	9.8	33.3	19.8		29.7	0.35	7.3

It should be noted that a limited number of waste forms were fabricated with cerium sulfate in the waste simulant (per Table 3-2). These forms were evaluated only for water immersion testing since we determined that the use of cerium oxide would be appropriate to use as a surrogate.

3.3.2 Waste Forms for TCLP and ANS 16.1 Test

The TCLP and ANS 16.1 tests were conducted on waste forms fabricated with hazardous elements in the waste streams, as per the instructions provided in the waste stream formulations by CNS. Waste streams were fabricated with the requisite amounts of hazardous contaminants added. The hazardous contaminants and their concentrations were as follows: As (<35 ppm), Ba (<650 ppm), Cd (<330 ppm), Cr (<1000 ppm), Pb (<125 ppm), Hg (<10 ppm), Se (<75 ppm), and Ag (<15 ppm). The radionuclide surrogate (Ce) was ~60,000 ppm. The various RCRA metals were added in their soluble compounds as follows: $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, Se_2O_3 , and AgNO_3 .

Since the concentrations of the RCRA metals were quite low, to reduce the uncertainty in measuring the RCRA metal compounds, a stock solution was prepared with concentrations of the metals 100X more than the desired levels. Figure 3-5 shows the stock solution with pH of 0.72. To fabricate waste forms, the stock waste solution was diluted by 100X prior to fabricating the waste forms as described in Section 3.3.1. Further, for mercury stabilization, 0.2 wt.% (of the dry powder mix) of potassium sulfide was added to the waste simulant and mixed until it dissolved.

After the waste forms were cured for 2-3 weeks, samples were extracted from plastic molds and shipped to GEL Laboratories (Charleston, South Carolina) for TCLP testing. GEL Laboratories crushed the samples as per the standard to perform the TCLP tests. For ANS 16.1 tests, samples were fabricated in cylindrical form of the desired dimensions and were tested in their solid form.

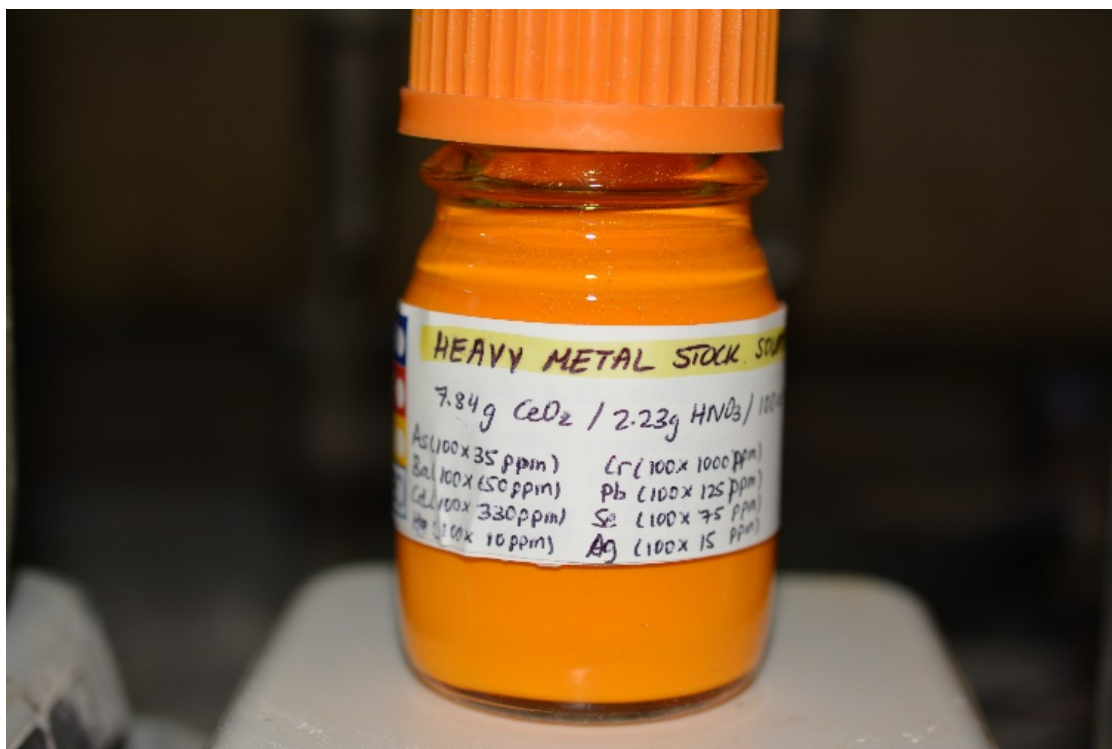


Figure 3-5. Waste simulant stock solution containing RCRA metals 100X the target value of the actual waste

4 PHYSICAL PROPERTY CHARACTERIZATIONS

4.1 Expansion Evaluation

After curing, the blank and the waste form samples were removed from the plastic syringe molds and sliced into appropriate lengths for various evaluations. Figures 4-1 and 4-2 show a typical sample with Class C fly ash and CaSiO_3 fillers. After the slurry was poured into the syringe, a mark was made to keep track of any expansion that occurs during the two-week curing. After at least two weeks of curing, the samples were removed from the plastic syringes and cut in appropriate sizes (approximately 1 in. in length) for subsequent characterizations.

Figures 4-1 and 4-2 indicate no discernible expansion in the waste forms after setting. The set product was at the same length, indicating no expansion. Most of the other samples exhibited no expansion or shrinkage. There was no evidence of any segregation.

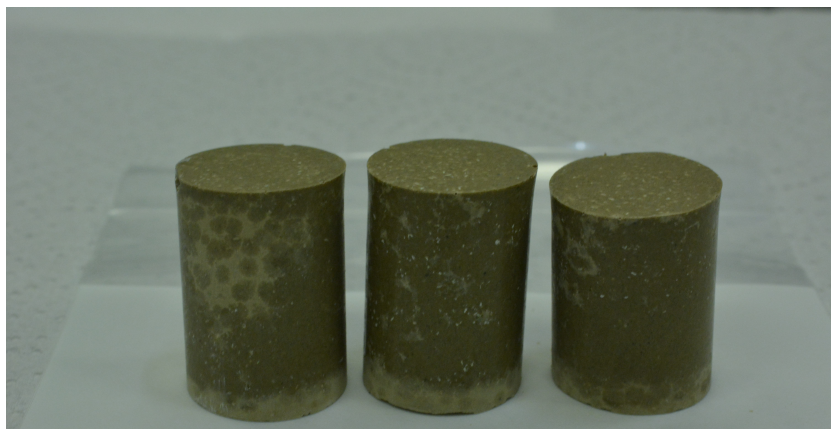


Figure 4-1. As-fabricated waste form for ~30 wt.% Class C fly ash and 25 wt.% waste simulant

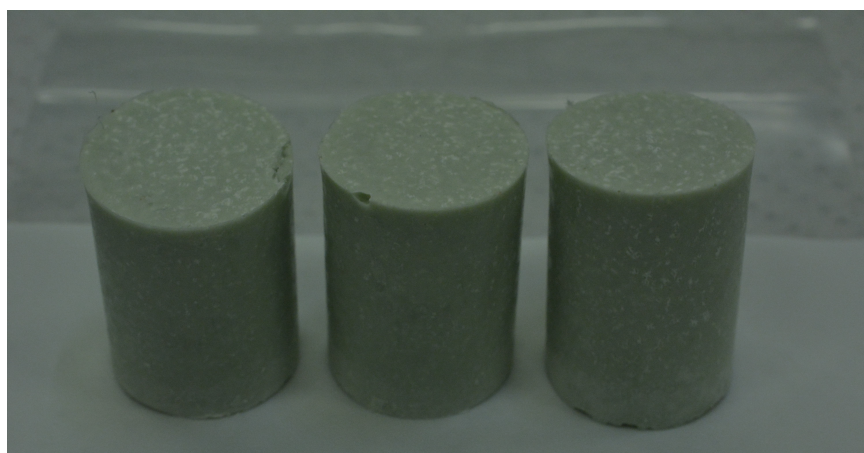


Figure 4-2. As-fabricated waste form for ~30 wt.% CaSiO_3 and 20 wt.% waste simulant

4.2 Density

Densities of the fabricated samples were calculated from the ratio of the sample weight and its volume. The volume of each sample was calculated from measurements of sample diameter and length. Typically, 2-3 samples of each formulation were used to determine the average density. Table 4-1 lists the average densities of the various waste forms fabricated. For the most part, the densities ranged from 1900 to 1980 kg/m³.

Table 4-1. Density of waste forms fabricated using baseline waste simulant

Sample Composition	Average Density, 10 ³ (kg/m ³)
FA+15W	1.9221 ± 0.010
FA+20W	1.9204 ± 0.009
FA+25W	1.885 ± 0.033
CaSi+15W	1.9797 ± 0.008
CaSi+20W	1.9820 ± 0.008
CaSi+25W	1.9698 ± 0.010

4.3 Compressive Strength of As-fabricated Samples

Compressive strength tests were conducted with cylindrical samples of 0.5-in. diameter and 1.0-in. length. Tests were conducted under a standard laboratory atmosphere on a Model 4505 Instron Universal Testing System, shown in Fig. 4-3. The loading rate was 1 mm/min. Loads versus cross-head displacements were recorded. Compressive strength was calculated by measuring the peak load at failure and dividing by the initial sample cross-sectional area. For each formulation, at least three samples were tested, and an average value was determined. The minimum compressive strength requirement for the waste forms is 500 psi [9].

Figures 4-4 through 4-6 show the compressive strengths measured for the baseline samples with varying waste stream loadings and filler proportions (see also Appendix A, Table A-1). Since the strength of the waste forms is expected to increase with time as the curing continues, for a specific waste form composition, strengths were measured at approximately 15-30 days of curing. Figure 4-4 shows the compressive strengths of the fly ash and CaSiO₃ filler-based waste forms. For both cases, at 25 wt.% loading, the strength is smallest. The compressive strengths of CaSiO₃ waste form are significantly superior to those of the fly-ash-based waste forms. For the most part, the strengths are >2000 psi.

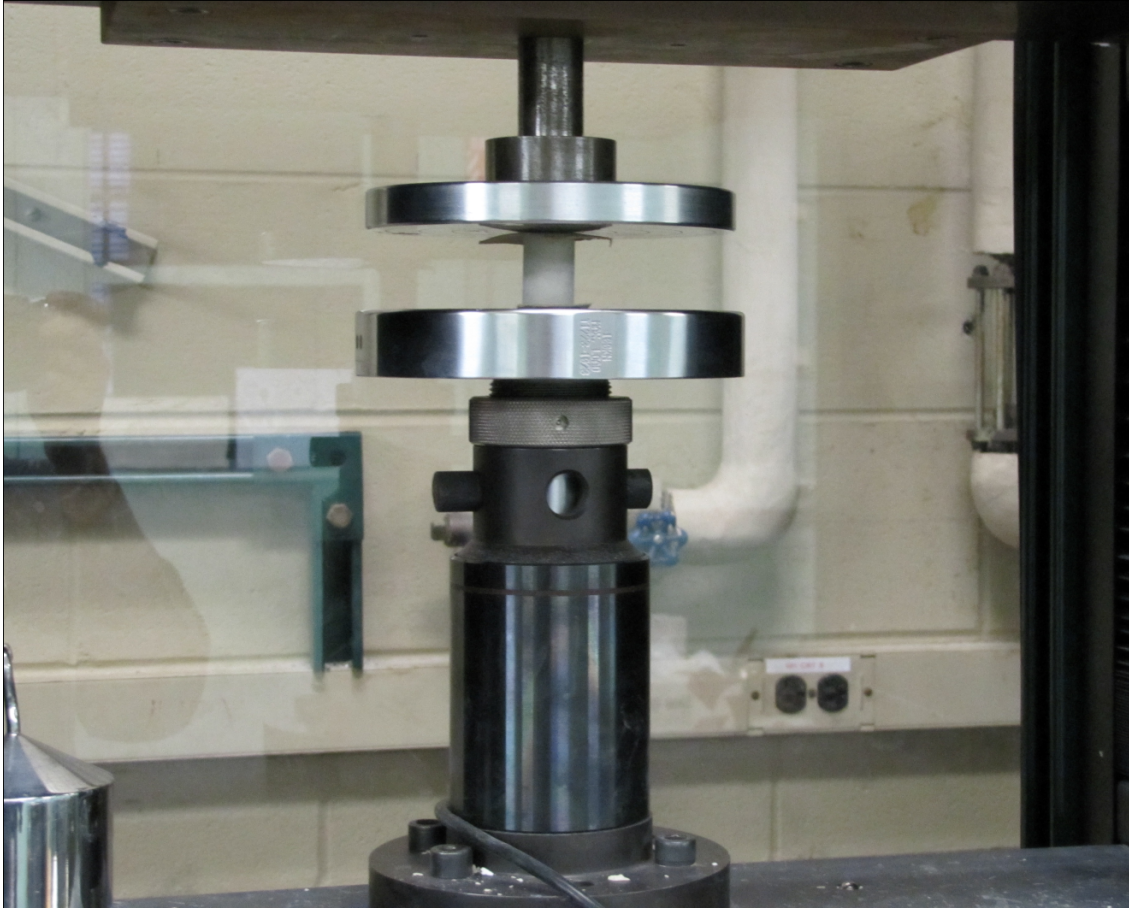


Figure 4-3. Test setup on Instron for measurement of waste form compressive strength

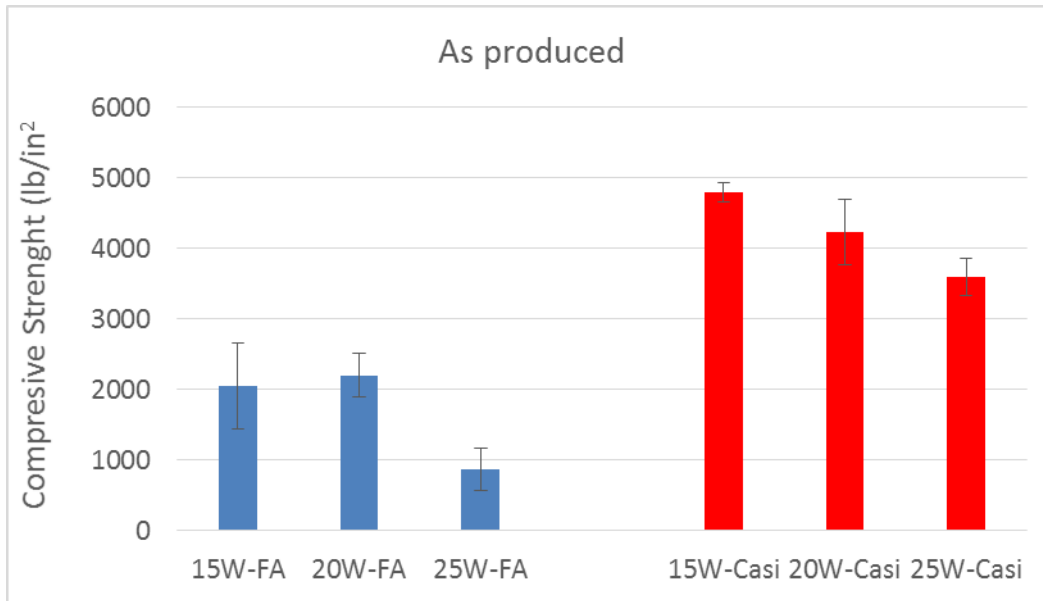


Figure 4-4. Compressive strength of waste forms with baseline waste simulant having fly ash and CaSiO_3 fillers

4.4 Summary

1. Density of the fabricated waste forms was 1.89-1.98 g/cc.
2. On average, waste forms with CaSiO_3 filler performed slightly better in compressive strengths as compared to those with the fly ash.
3. Compressive strengths of the waste forms fabricated with simulants (up to 25 wt.% waste loading) showed strengths > 2000 psi, independent of the filler material.

5 WATER IMMERSION TEST

Water immersion tests were conducted on samples from the same batch that were used for the strength evaluations, for which the samples were not immersed in water. For each composition, nine samples were placed in water. At the end of approximately 1, 2, and 3 months, the samples were retrieved, dried, weighed, and tested for compression strength. In addition to the compressive strengths, weight loss of the waste forms as a function of water exposure time was monitored. This test provides insight into the stability of the waste forms.

5.1 Waste Form Appearance

Once the waste forms were exposed for the requisite time in water, they were wiped dry in a hood and inspected for white residue formation or cracking in the sample. Figures 5-1 through 5-6 are representative photographs of the waste forms fabricated using either fly ash or CaSiO_3 as the filler and waste loadings of 15-25 wt.%. Further, the appearance of the as-fabricated samples and samples after exposure times of 1, 2, and 3 months is shown. These waste forms did not have any RCRA metals.

As can be seen in the figures, no residue was observed on the waste form surface. In addition, there are no cracks or sign of degradation of the waste forms after 3 months of the water immersion test.

5.2 Weight Loss Measurements

As part of the water immersion testing, weight loss of the samples at 1, 2, and 3 month intervals was monitored in separate sets of samples. After each interval, samples were cleaned with wipes and were allowed to air dry for several days in a hood. Then, percent weight loss of the sample was determined. The 1- and 2-month samples were returned for continued water immersion testing. The tests were done in triplicate at each condition.

Figures 5-7 through 5-12 show the weight loss for the various waste forms fabricated using the two filler materials: fly ash and CaSiO_3 (see also Appendix B). It should be noted that the weight losses reported for different immersion times are on different samples that were left undisturbed. For the fly ash and CaSiO_3 samples, waste loadings were 15 wt.%, 20 wt.%, and 25 wt.%.

The results show that during the first month, the weight loss is the highest, 2-3 wt.%. This weight loss is probably due to unreacted binder powders on the surface of the waste form being removed. There is not much weight change for the samples immersed for 2 and 3 months. Depending on the sample composition, there is approximately 2-3 wt.% change during the subsequent 2-month period, indicating the waste form is stable.

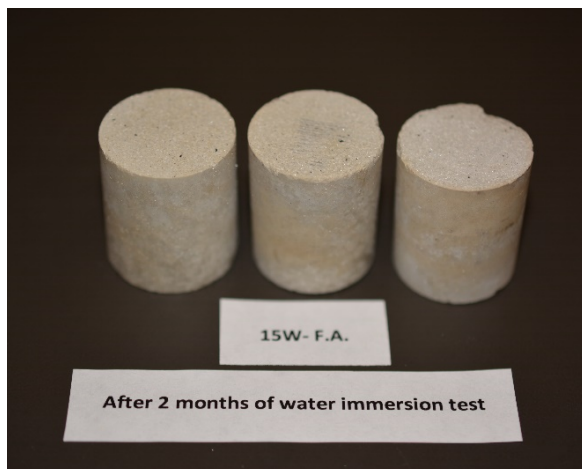
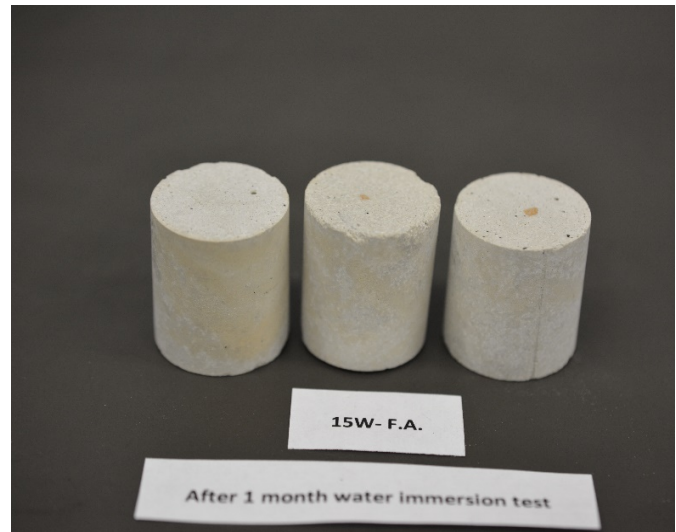
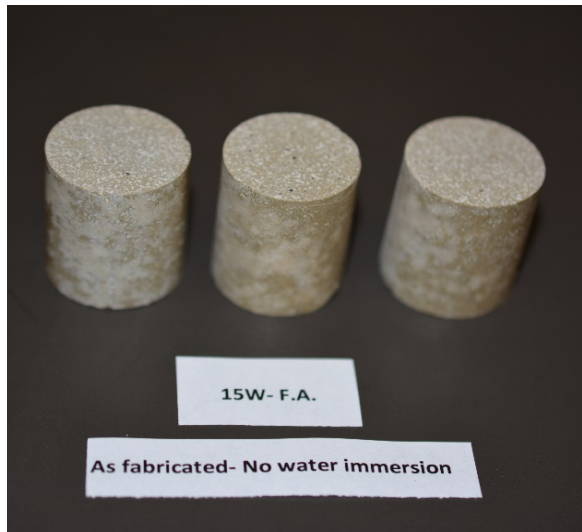


Figure 5-1. Waste form samples with 15 wt.% waste simulant loading and fly ash filler: (a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing

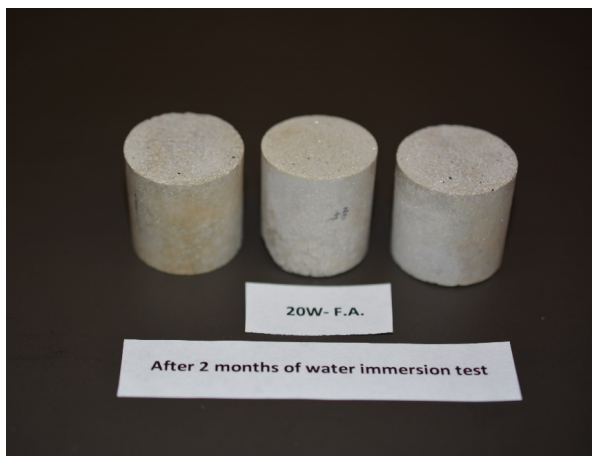
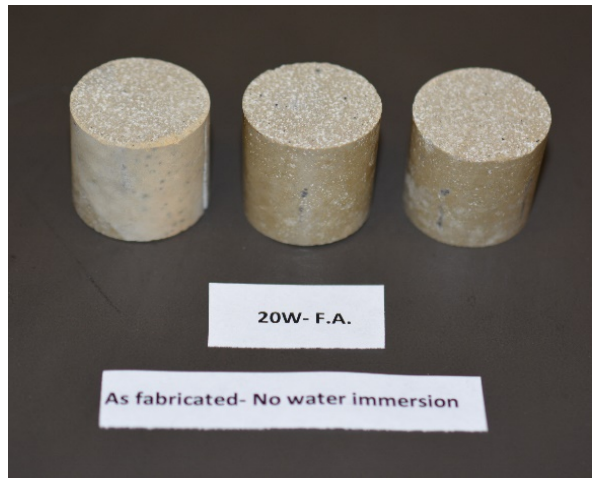


Figure 5-2. Waste form samples with 20 wt.% waste simulant loading and fly ash filler:
(a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing

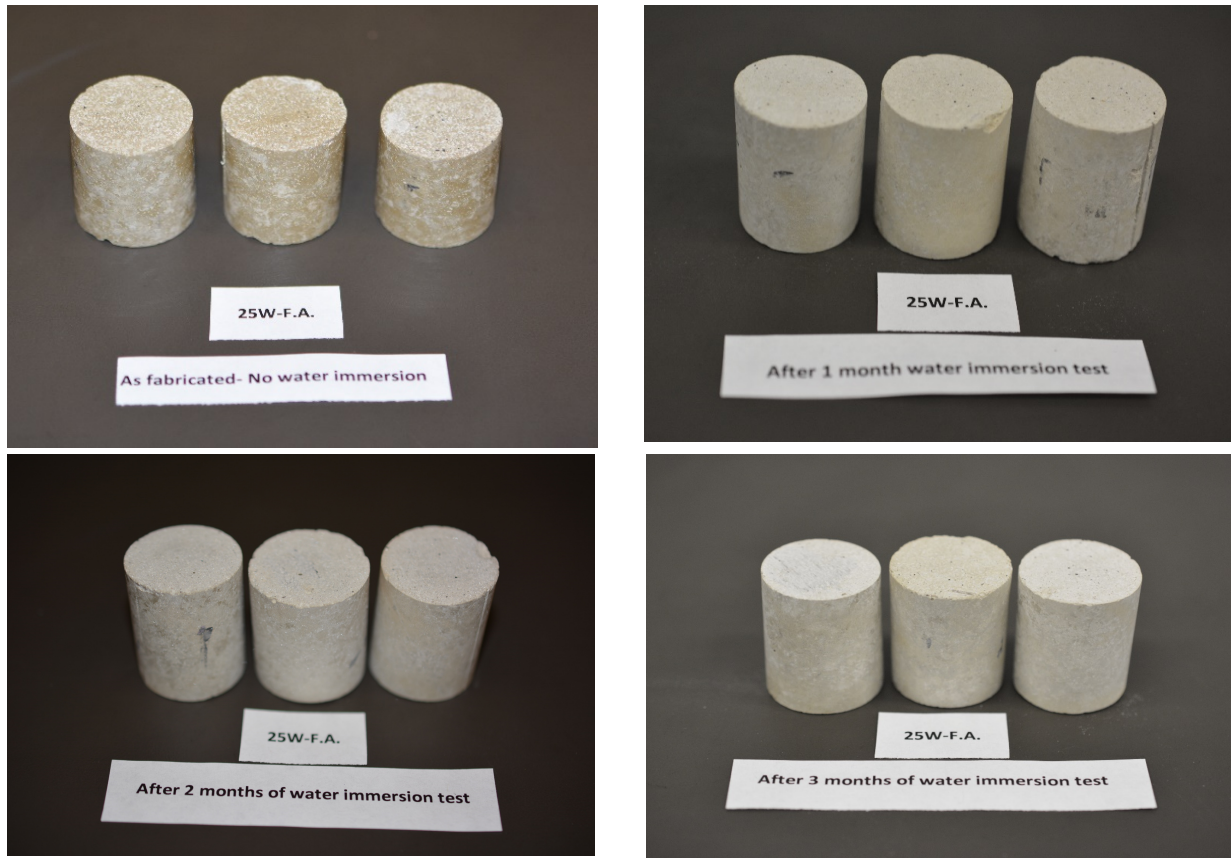


Figure 5-3. Waste form samples with 25 wt.% waste simulant loading and fly ash filler:
(a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing

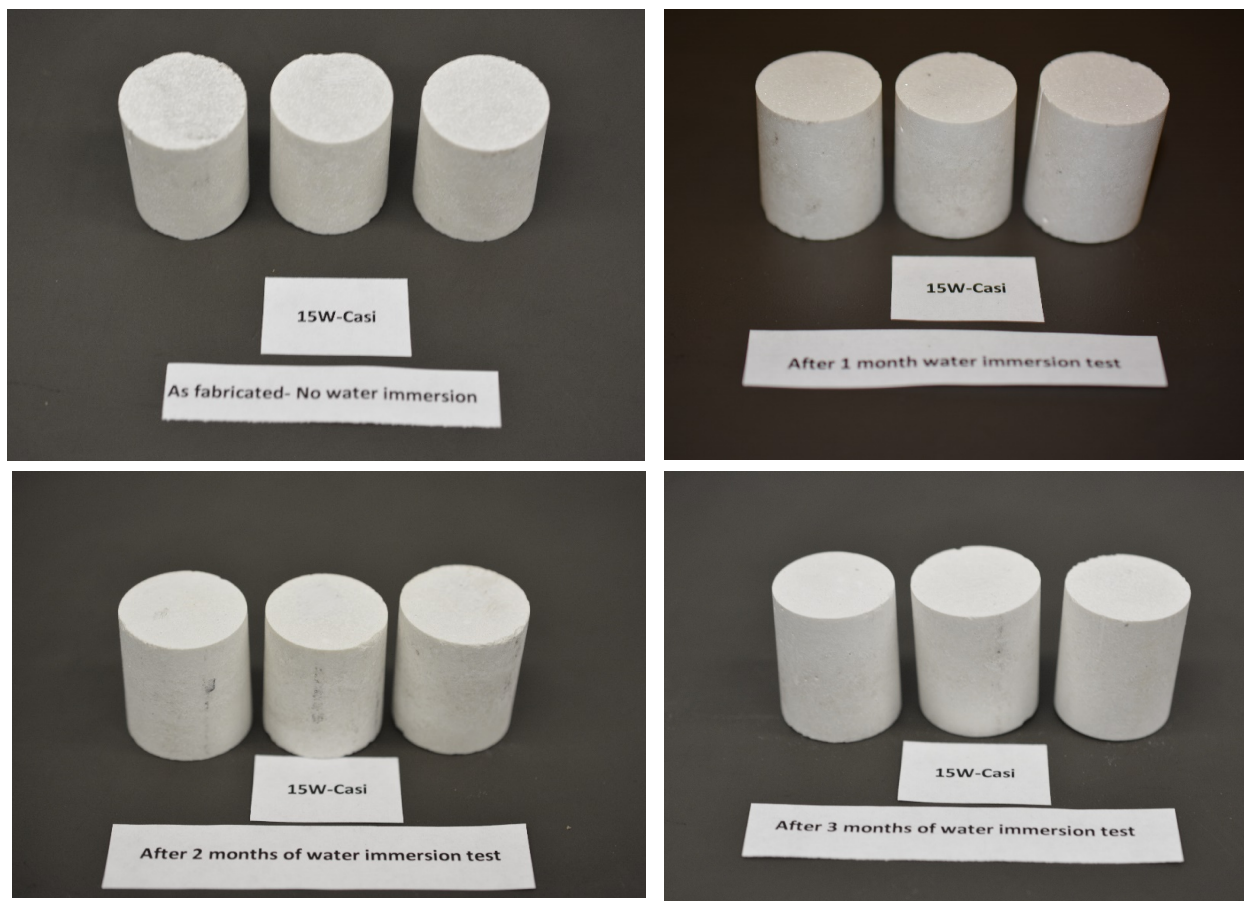


Figure 5-4. Waste form samples with 15 wt.% waste simulant loading and CaSiO_3 filler:
(a) as-fabricated and sfter (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing

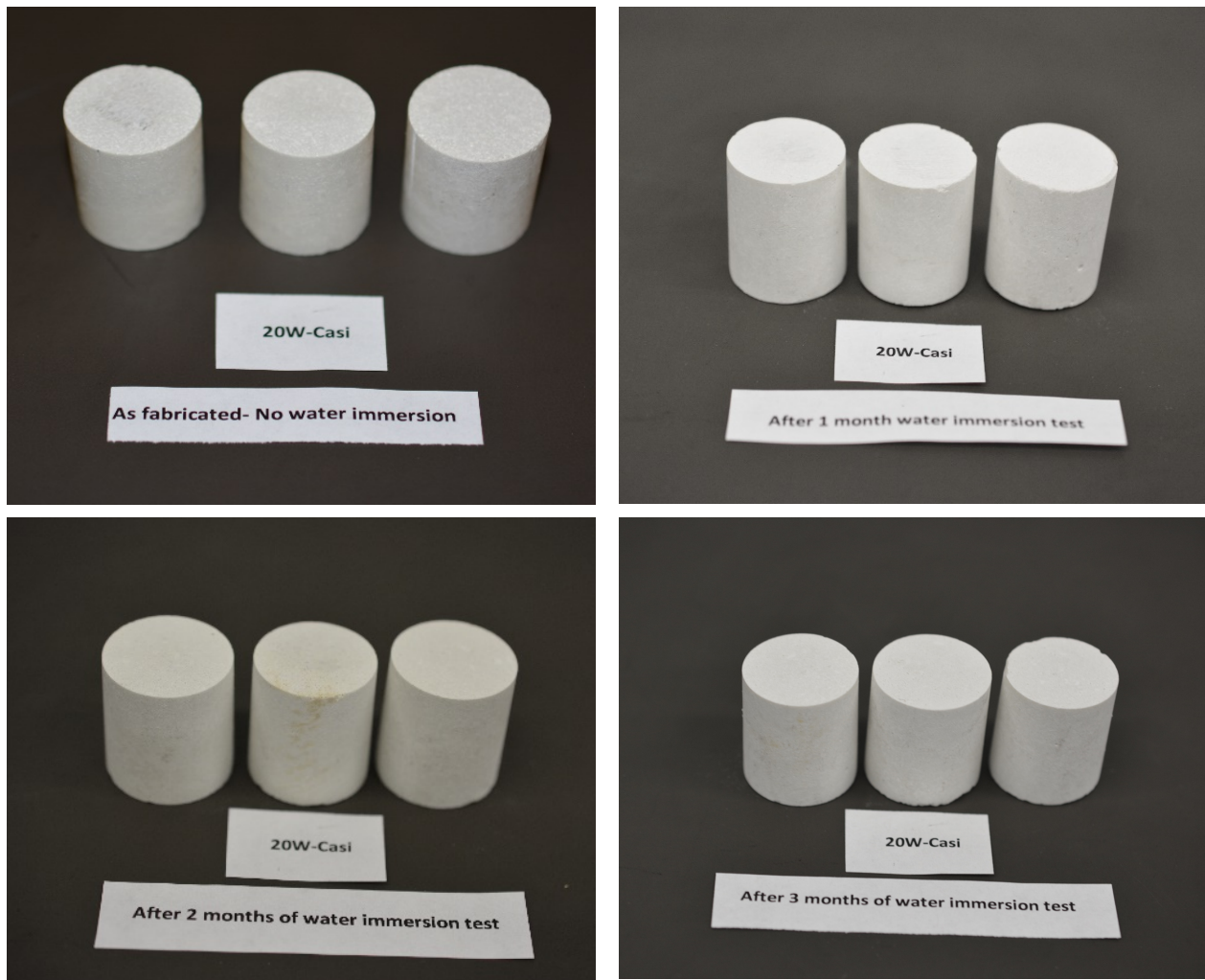


Figure 5-5. Waste form samples with 20 wt.% waste simulant loading and CaSiO_3 filler:
(a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing

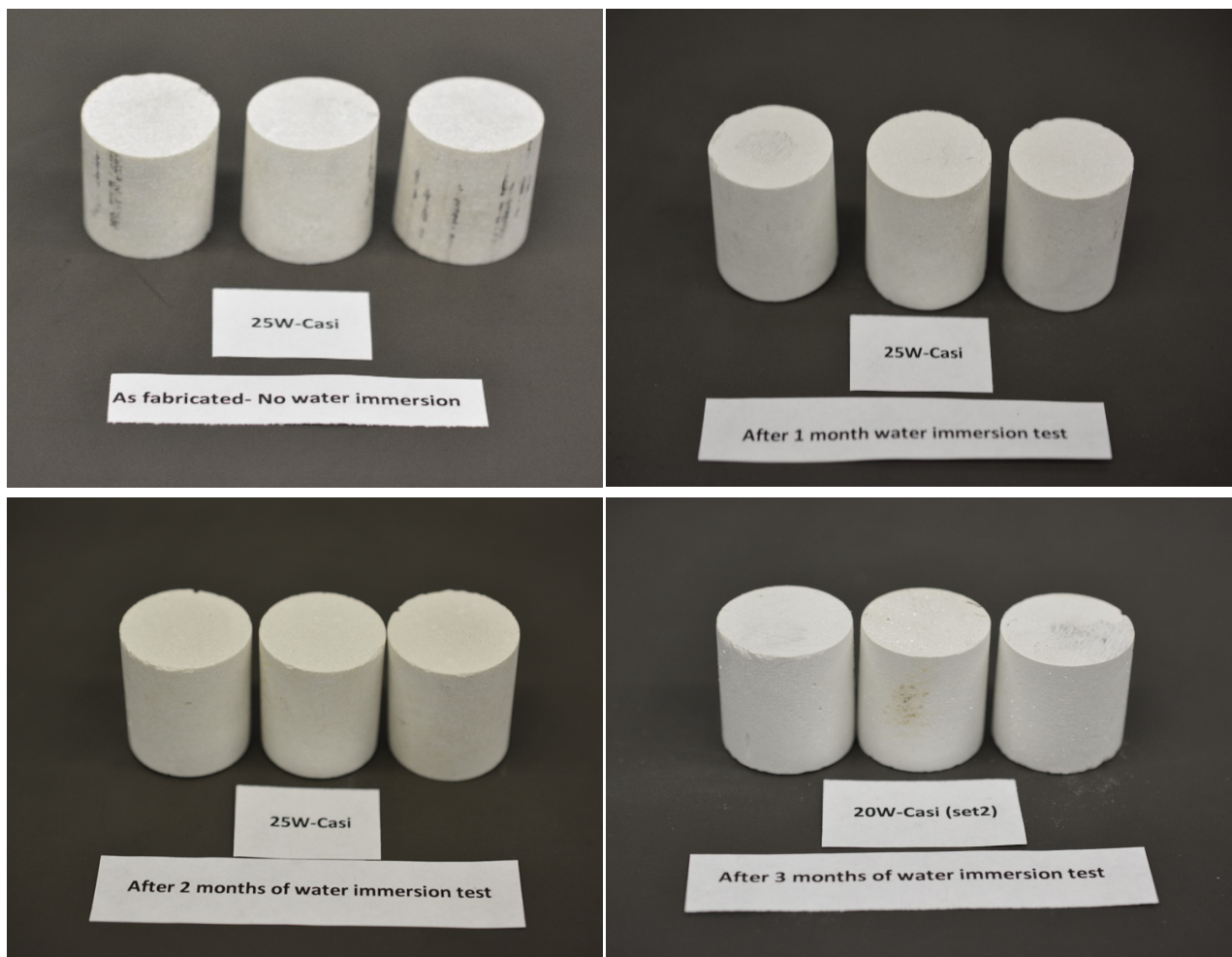


Figure 5-6. Waste form samples with 25 wt.% waste simulant loading and CaSiO_3 filler:
(a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing

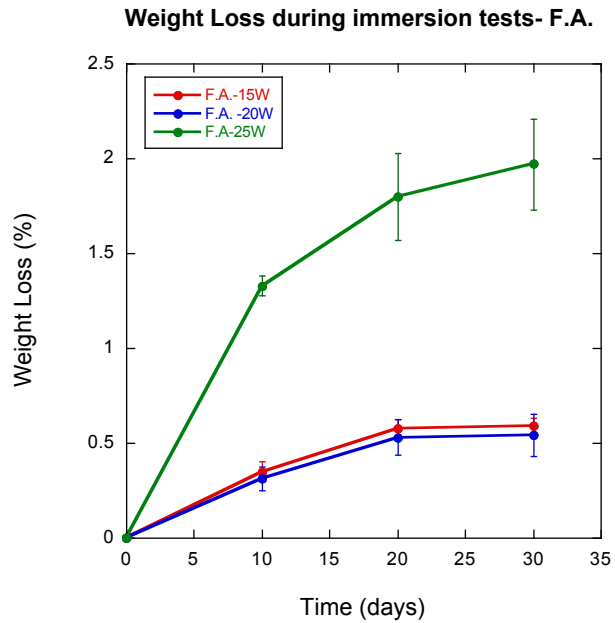


Figure 5-7. Weight loss of waste forms during 30-day water immersion for fly ash filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings

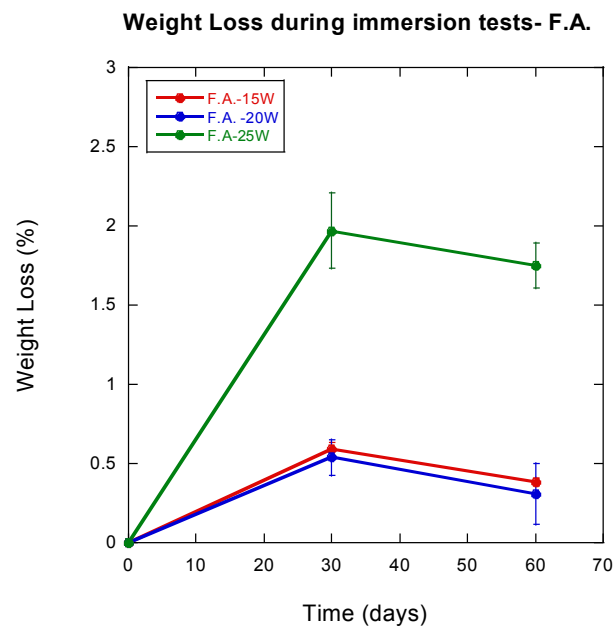


Figure 5-8. Weight loss of waste forms during 60-day water immersion for fly ash filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings

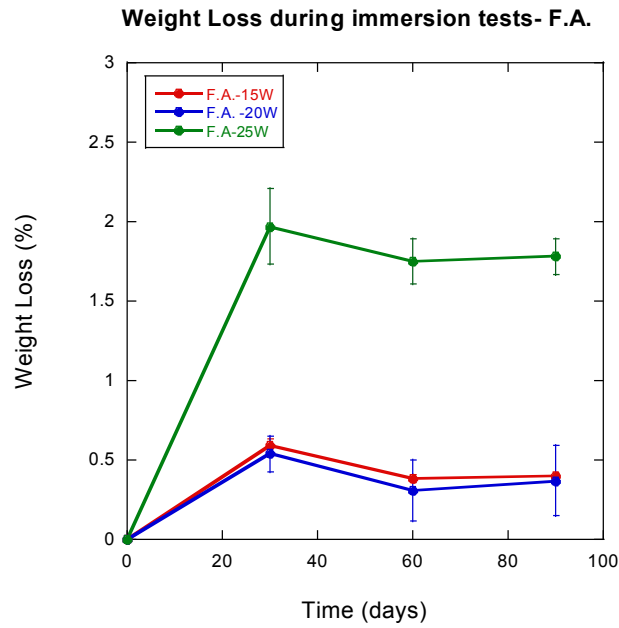


Figure 5-9. Weight loss of waste forms during 90-day water immersion for fly ash filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings



Figure 5-10. Weight loss of waste forms during 30-day water immersion for CaSiO_3 filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings

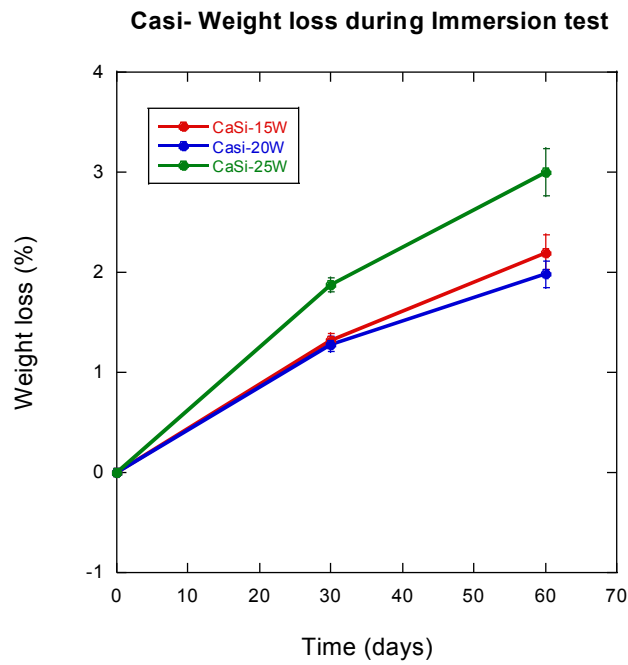


Figure 5-11. Weight loss of waste forms during 60-day water immersion for CaSiO_3 filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings

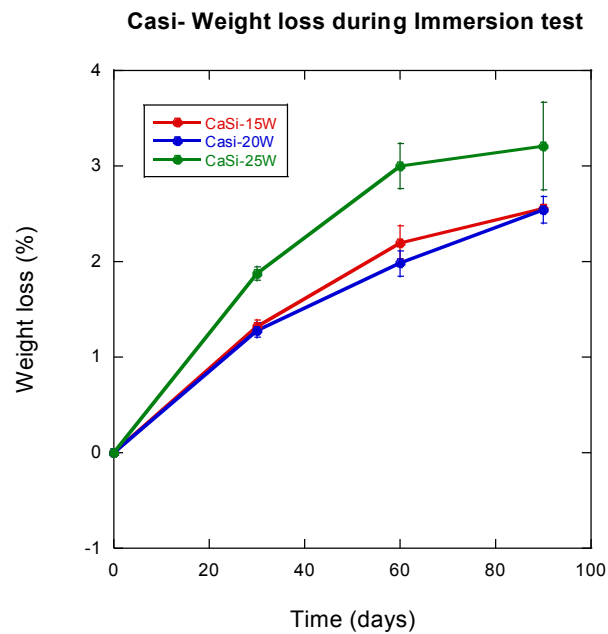


Figure 5-12. Weight loss of waste forms during 90-day water immersion for CaSiO_3 filler and 15 wt.% , 20 wt.%, and 25 wt.% waste loadings

5.3 Compression Strength

Compression tests on the water-exposed samples were conducted in the same manner as for the as-fabricated samples described in Section 4.3. Compression strengths measured from the water immersion tests are shown in Figures 5-13 and 5-14 for various wastes loadings and filler type (see also Appendix A, Table A-2). For the fly ash filler waste forms, the strengths do not degrade with immersion time. In fact, the strength increases for the 25 wt.% waste loading sample. This behavior has been observed in our previous work [2] and is attributed to the further curing of the binder phase.

Figure 5-14 shows a similar plot of the compressive strengths as a function of immersion time for the CaSiO_3 filler material. Here again, there is no apparent degradation observed for the waste forms for the 3-month exposed samples as compared to the as-fabricated strengths.

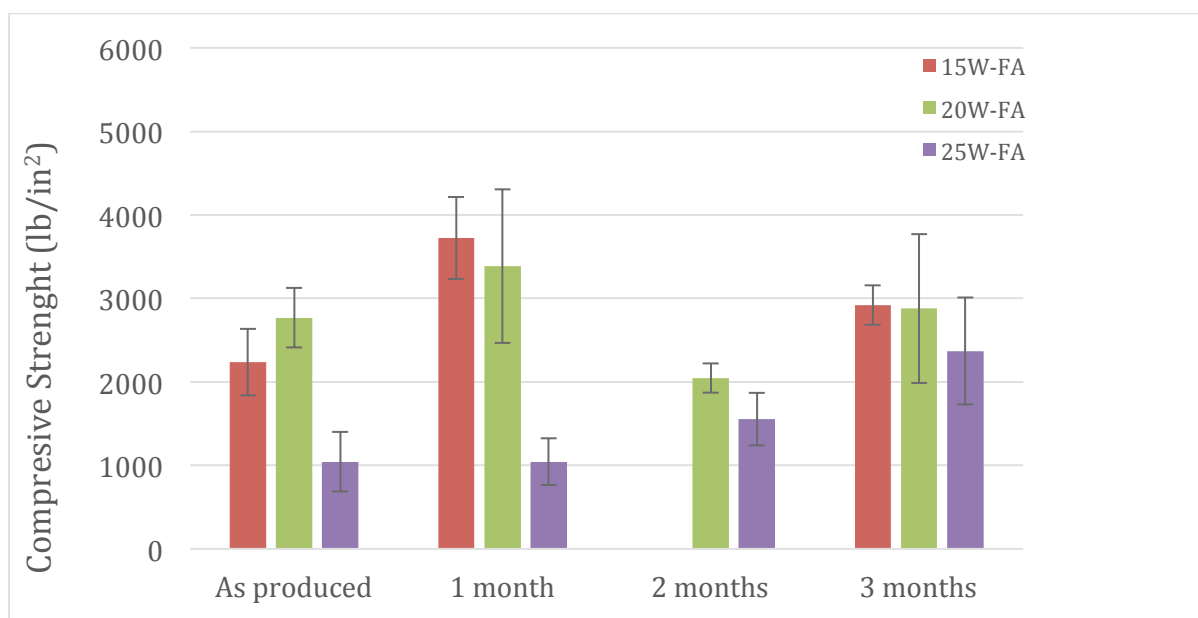


Figure 5-13. Compressive strength of waste forms with various waste loadings and fly ash filler as a function of immersion time

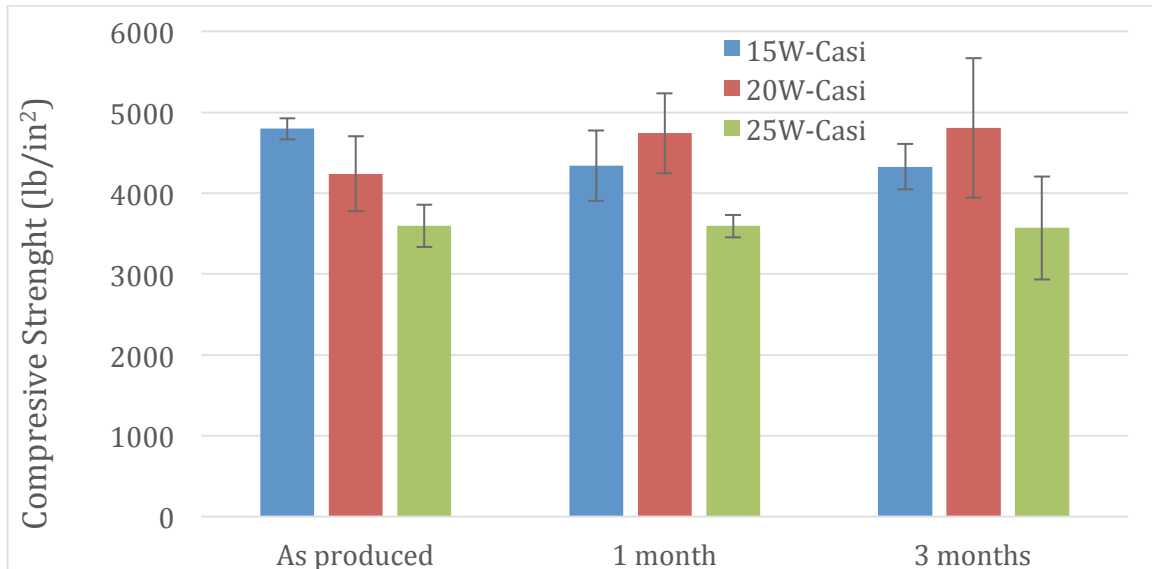


Figure 5-14. Compressive strength of waste forms with various waste loadings and CaSiO_3 filler as a function of immersion time

5.4 Water Immersion Testing of Waste Forms Fabricated Using Cerium Sulfate as Surrogate

As mentioned before, limited samples were fabricated where cerium sulfate was used as surrogate for uranium. These waste forms were evaluated only for water immersion tests. Figures 5-15 and 5-16 show the waste forms fabricated with fly ash and CaSiO_3 as fillers and with different testing times. For both sets of waste forms, even after 3 months of testing, no visible degradation was observed.

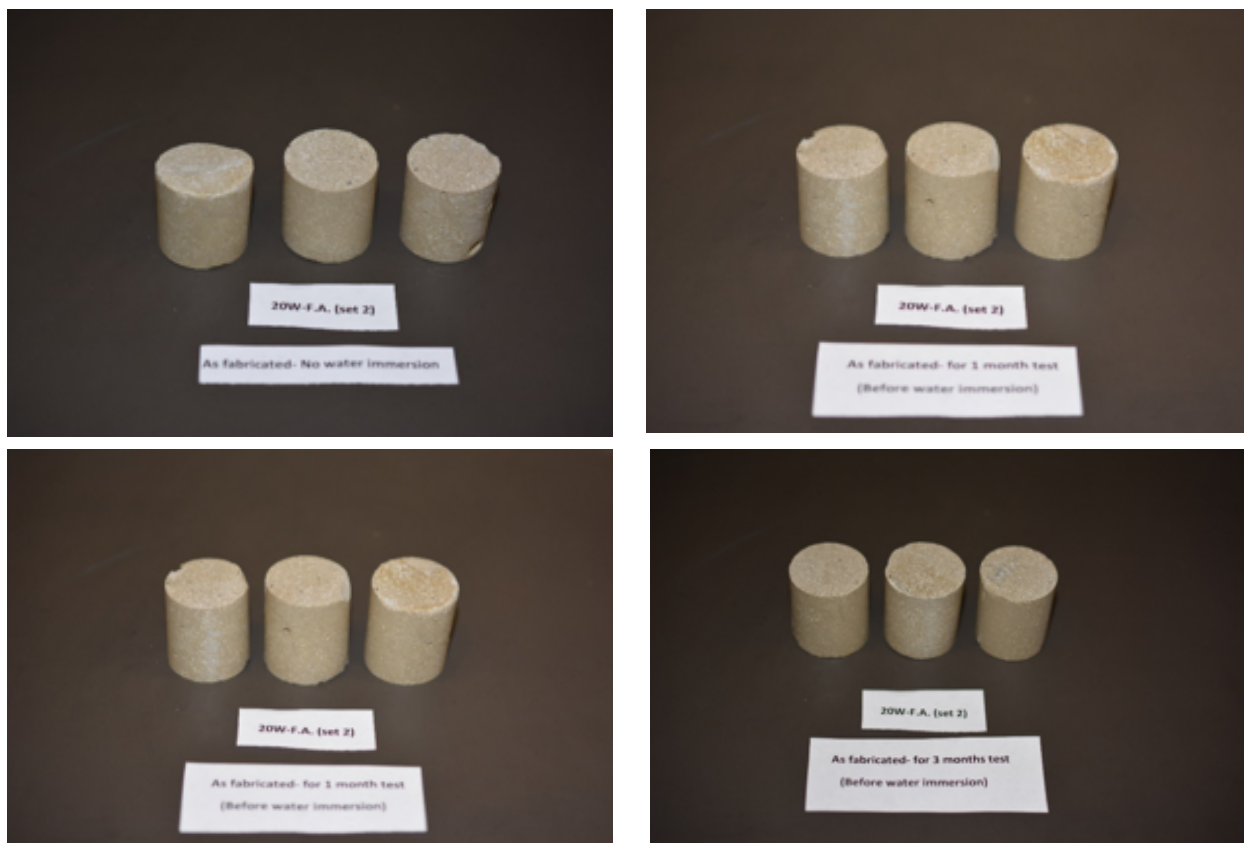


Figure 5-15. Waste form samples with 20 wt.% waste simulant loading and fly ash filler: (a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing. Cerium in form of cerium sulfate was used as surrogate for uranium

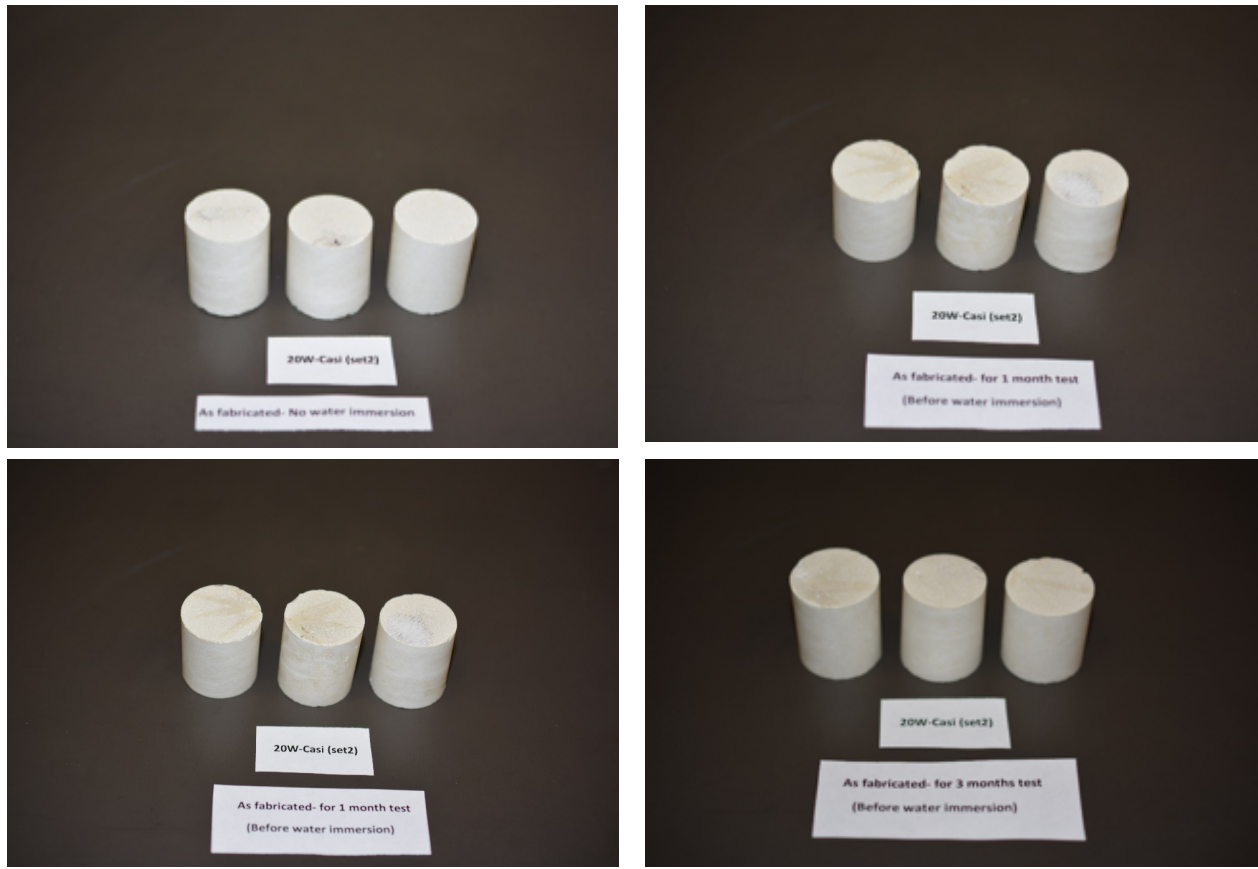


Figure 5-16. Waste form samples with 20 wt.% waste simulant loading and CaSiO_3 filler: (a) as-fabricated and after (b) 1 month, (c) 2 months, and (d) 3 months of water immersion testing. Cerium in form of cerium sulfate was used as surrogate for uranium

Figure 5-17 shows the weight loss for the waste forms fabricated with cerium sulfate as the surrogate for uranium. Samples with 20 wt.% waste loadings were evaluated. For both sets of waste forms with fly ash and CaSiO_3 fillers, weight loss was about 1-3% during the first month of exposure. For the next two months, the weight loss was minimal. Further, similar to the waste forms with cerium oxide used as the surrogate, the fly-ash-based waste forms performed somewhat better than those fabricated with CaSiO_3 as filler.

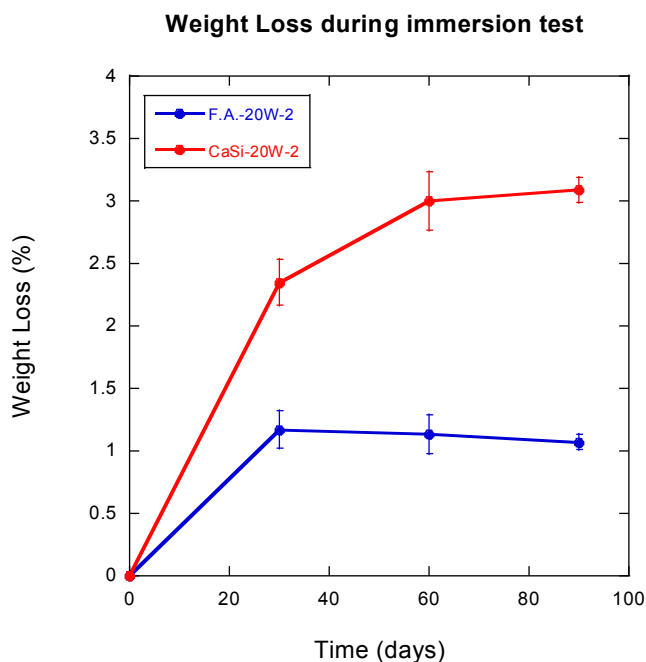


Figure 5-17. Weight loss of waste forms during 90-day water immersion for fly ash and CaSiO_3 fillers with 20 wt.% waste loading

5.5 Summary

Weight loss of the waste forms was measured on samples immersed in water for 1, 2, and 3 months to determine the stability of the waste forms. The waste forms contained different filler materials (fly ash and CaSiO_3) and had waste loadings of 15, 20, and 25 wt.%. The following conclusions were reached from the weight loss data:

1. The majority of the weight loss (~2-3 wt.%) occurred in the first month of the test period. This loss is probably due to residual unreacted MgO and potassium phosphate on the waste form surface that washed off.
2. Subsequent immersion time intervals (2 and 3 months) did not show any additional significant drop in the weight loss over the first one-month water immersion. There was no discernible difference in the weight loss per the filler type used for the waste form fabrication.
3. Overall, the waste forms appeared to be stable over the 3-month water immersion tests. No evidence was found of any surface residue buildup.
4. The compressive strengths of the water-immersed samples were similar or even increased with time as compared to the as-fabricated samples for the same filler and waste loading. The increased strength with immersion time can be attributed to the curing of the binder phase.
5. Waste forms fabricated with cerium sulfate as the surrogate were equally stable to those with cerium oxide after the 90-day water immersion test.

6 AMERICAN NUCLEAR SOCIETY'S 16.1 LEACHING TEST

6.1 Leachability Index Determination

As per the ANS 16.1 test procedure, the leachability index (LI) for radionuclide species and surrogates is determined by conducting a test in which a cylindrical (1-in. length and 0.50-in. diameter) waste form sample is suspended in a known volume (10 times the surface area of the sample) of leachant. The water is replaced at fixed time intervals (2, 5, 17, 24, 24, 24, 24, 336, 672, and 1032 h) to simulate dynamic leaching conditions. The contaminant species, n , in the leachate were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). The effective diffusivity (D_e) and leachability index (LI) are given by

$$D_e = \pi[(a_n/A_o)/(\delta t)_n]^2(V/S)^2(T)$$

$$LI = (1/n)\Sigma[\log(b/D_e)]_n$$

In the above equations, a_n represents the amount (g) of contaminant leached from the waste form during the leaching interval n ($t_{n-1} < t < t_n$), A_o is the amount of contaminant in the waste form at the beginning of the leach test (g), $(\delta t)_n (= t_n - t_{n-1})$ is the duration of the n^{th} leaching interval (s), D_e is the effective diffusivity (cm^2/s), V is the volume of the waste form (cm^3), S is the external surface area of the waste form (cm^2), T is the mean time of the leaching interval (s) and is represented as $[0.5(t_n^{1/2} + t_{n-1}^{1/2})]^2$, and b is a constant ($1 \text{ cm}^2/\text{s}$).

Based on the waste loadings for the various ANS 16.1 samples and the compositional make-up of each sample type, initial amounts of specific species, A_o , in the waste form at the start of the test were determined. The initial concentration used for the leachability index (LI) calculation was corrected for the amount of the specific species lost during the initial “rinse” step of the test protocol.

Tables 6-1 and 6-2 present the leachability indices for the samples evaluated in duplicates. Two waste loadings (20 wt.% and 25 wt.%) were evaluated with both fly and CaSiO_3 fillers. Leachate solutions were not only analyzed for the radioactive surrogate, Ce, but also for Mg, P, Si, and the RCRA elements. It is recognized that the hazardous elements are not required per the ANS 16.1 test protocol. The LI of the non-radioactive surrogates provides insight into the stability of the waste form itself. The higher the leachability index, the better is the waste form in retaining the specific element. Typically, LI of >6 is considered acceptable. Further, since LI is defined as a logarithm of inverse of diffusivity (equation above), an increase in LI by 1 implies the reduction in the diffusivity by a factor of 10. Appendix C presents the diffusivity values for the various species at each leach interval for selected waste forms.

Results in Table 6-2 are for tests conducted for 60 days, since the 90-day test sample had not been analyzed at the time of the preparation of the report.

Table 6-1. Average leachability indices of key elements from
ANS 16.1 tests conducted on various waste forms^a

Waste form	Mg	Si	P	Ce
20%W+FA-1	18.4	18.3	29.4	30.4
20%W+FA-2	17.8	19.8	29.4	30.5
25%W+FA-1	17.6	19.3	29.4	30.4
25%W+FA-2	18.4	18.3	29.4	30.4
20%W+CaSiO3-1	30	17.3	29.1	31.3
20%W+CaSiO3-2	30.2	17.4	29.3	31.2
25%W+CaSiO3-1	30.4	16.8	29.5	31.3
25%W+CaSiO3-2	30.3	16.8	29.4	31.2

^aResults reported are based on 60-day tests

Table 6-2. Average leachability indices of RCRA metals from ANS 16.1 tests
conducted on various waste forms^a

Waste form	Cr	As	Se	Ag	Cd	Ba	Pb
20%W+FA-1	25.6	25.2	24.0	30.7	27.8	29.3	29.4
20%W+FA-2	25.2	25.2	23.9	30.6	27.7	29.2	29.4
25%W+FA-1	24.3	25.2	23.9	30.6	27.7	29.2	29.4
25%W+FA-2	24.0	24.5	23.7	30.6	27.7	29.4	29.4
20%W+CaSiO3-1	27.2	24.6	24.5	30.8	29.5	29.8	29.1
20%W+CaSiO3-2	27.1	24.6	24.5	30.7	30.2	30.2	29.3
25%W+CaSiO3-1	27.1	24.1	24.4	30.7	30.0	29.4	29.5
25%W+CaSiO3-2	27.3	24.1	24.4	30.7	30.2	30.1	29.4

^aResults reported are based on 60-day tests

6.2 Analysis of Waste Forms after ANS 16.1 Test

After the 90-day tests, the waste form samples were removed and analyzed. Figures 6-1 to 6-4 show the post-90-day ANS 16.1 samples with the both fly ash and CaSiO_3 fillers and waste loadings of 20 and 25 wt.%. As seen from the photographs of the three samples at each condition, no degradation/cracking occurred. These results are consistent with the weight loss measurements after the water immersion test. These results attest to the durability of the waste forms.

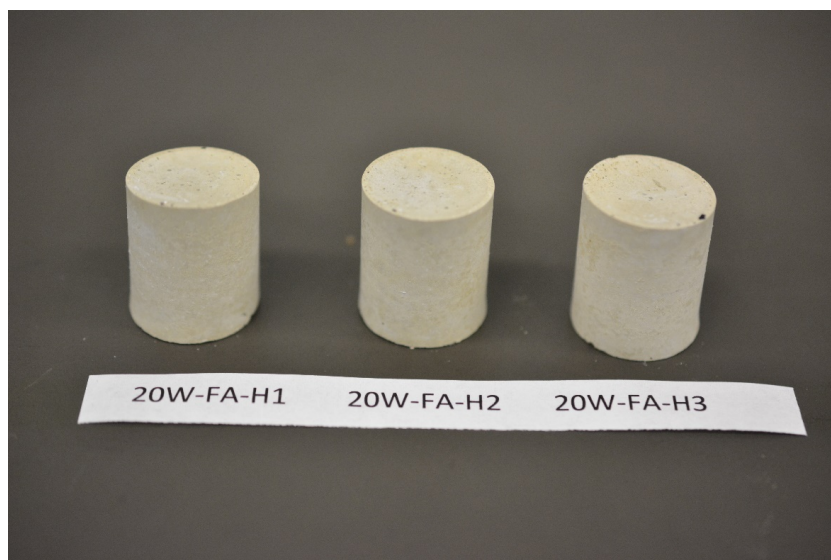


Figure 6-1. Samples with 20 wt.% waste loading and fly ash filler after 90-day ANS 16.1 test

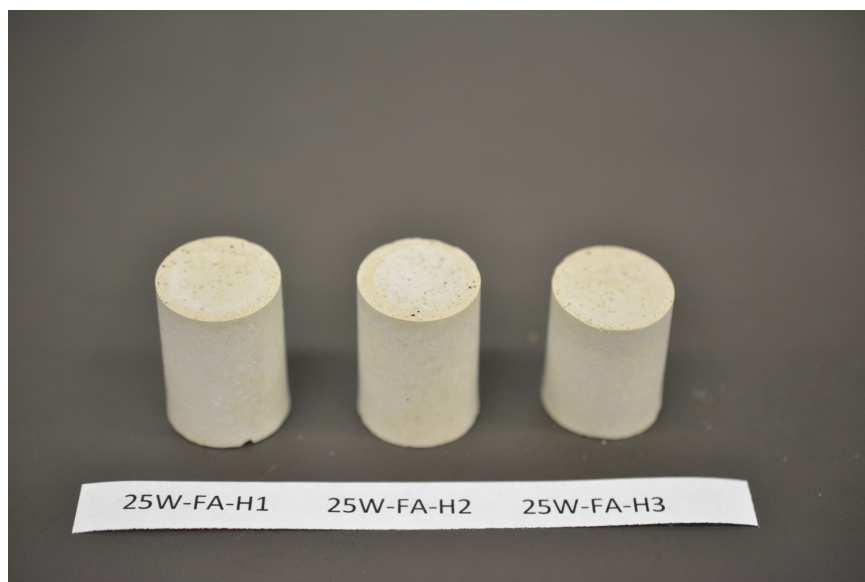


Figure 6-2. Samples with 25 wt.% waste loading and fly ash filler after 90-day ANS 16.1 test

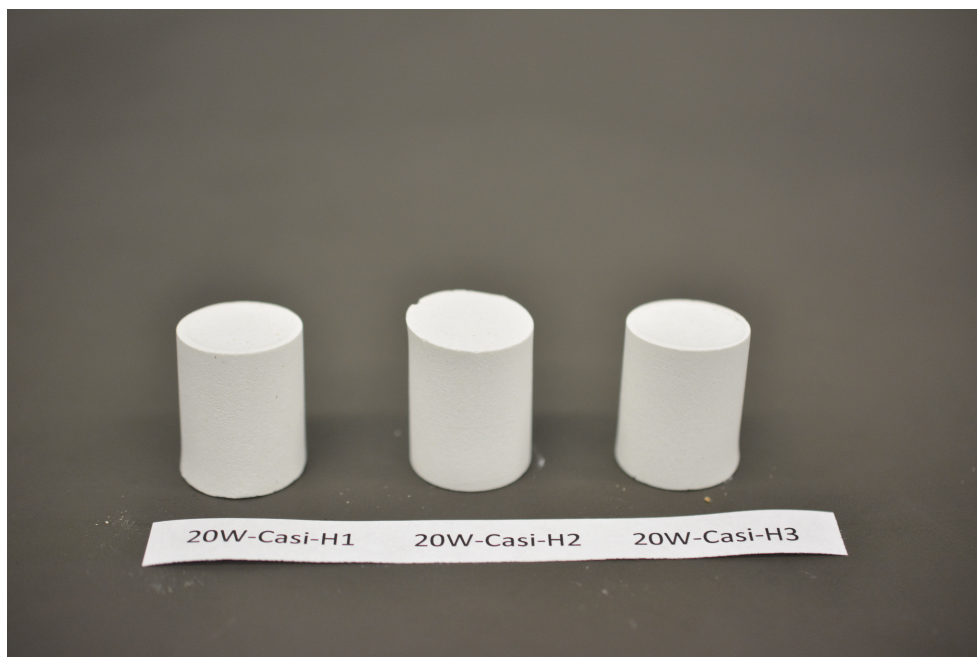


Figure 6-3. Samples with 20 wt.% waste loading and CaSiO_3 filler after 90-day ANS 16.1 test

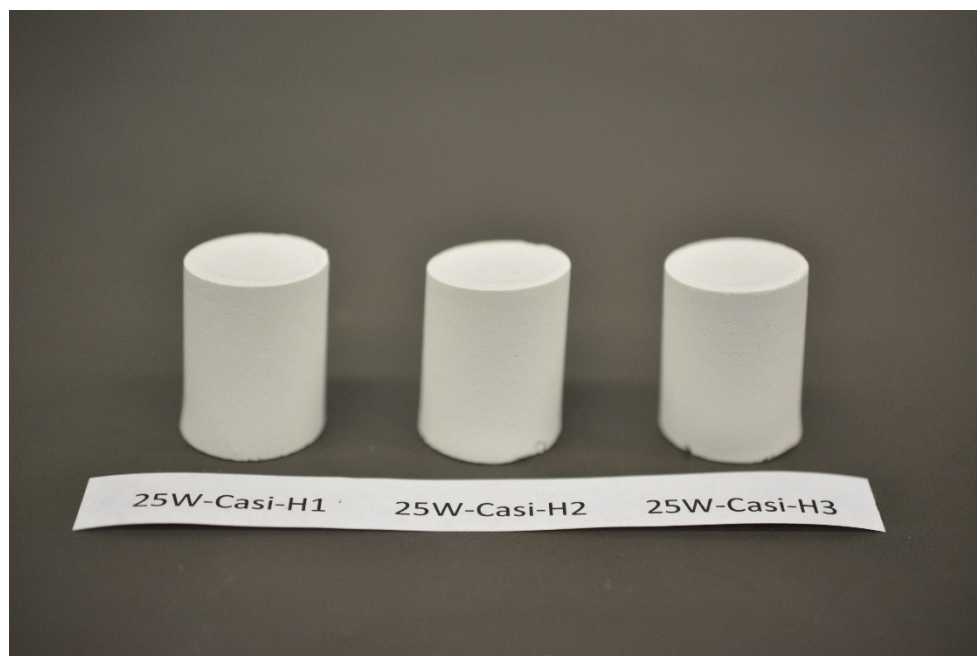


Figure 6-4. Samples with 25 wt.% waste loading and CaSiO_3 filler after 90-day ANS 16.1 test

6.3 Summary

The following conclusions were reached from the ANS 16.1 tests:

- (a) The radionuclide surrogate cerium has an extremely high LI, indicative of its containment.
- (b) The LIs of the waste form matrix binder components (Mg, Si, and P) are >17 , indicative of a durable waste form.
- (c) The RCRA metals also had LIs that were >20 . There was no specific trend observed with respect to the waste simulant or the filler types.
- (d) Based on the ANS 16.1 tests, the waste forms are successful in containing the radionuclide surrogate species (Ce) to as high as 25 wt.% waste simulant loadings.
- (e) After the 90-day ANS 16.1 tests, waste forms showed no visible degradation.

7 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

7.1 Analysis of Hazardous Contaminants in the Waste Simulants

Table 7-1 lists the concentrations of the various hazardous metals targeted in the waste streams as recommended by CNS. Also shown in the table is the cerium concentration in the waste simulant.

Table 7-2 shows the concentrations of the hazardous metals in the waste streams as determined by ICP-MS (ANL's Analytical Chemistry Lab). For very low concentrations of metal, there was a discrepancy in the targeted and observed concentrations. This discrepancy could be a result of the uncertainty in measuring very small amounts of metal salts (in tenths of a milligram). It should be noted that the Hg concentration was not measured in the waste simulant.

We analyzed the as-received fly ash for the RCRA metals to establish what contaminants are present in the fly ash and how they could possibly affect the overall metal concentrations in the waste forms. Table 7-3 shows the metal concentrations. Barium is a stand out and is found to be over 5000 ppm in the fly ash.

Table 7-4 lists the RCRA metal concentrations in the fabricated waste forms with the varying waste loadings. For the most part, concentration of the metals is proportional to the expected waste loading in the waste form. There are some discrepancies that could be attributed to the variability in the concentration of the RCRA metals in the waste simulants itself, although the waste solution was mixed thoroughly prior to using it for waste form fabrication.

Table 7-5 lists the TCLP results on the fabricated waste forms as provided by Gel Labs (see also Appendix D). The metal concentrations in the leachate are well below the UTS limits as shown in the table. In the case of Hg, the concentrations were below the detectable limits. Clearly, from the TCLP tests, containment of the RCRA metals is not an issue.

Table 7-1. Hazardous metal
and Ce concentrations targeted
in waste simulant

Elements	Concentration (ppm)
As	35
Se	75
Cr	1000
Ag	15
Cd	330
Ba	560
Pb	125
Hg	10
Ce	63300

Table 7-2. Hazardous metal concentrations in the in-house-prepared waste simulant

Elements	Concentration (ppm)
As	34.7
Se	36.6
Cr	878
Ag	12.9
Cd	214
Ba	783
Pb	108
Hg	^a
Ce	88259

^aNot measured

Table 7-3. Hazardous metal concentrations in the fly ash used for fabrication of the waste forms

Elements	Concentration (ppm)
As	21
Se	^a
Cr	104
Ag	1.47
Cd	1.57
Ba	5302
Pb	52
Hg	^a
Ce	145

^aNot measured

Table 7-4. Hazardous metal concentrations (ppm) in the fabricated waste forms

Sample	Description	As	Se	Cr	Ag	Cd	Ba	Pb	Hg	Ce
20%W+FA	20% waste loaded with fly ash as filler	11.3	7.6	208	2.21	45.6	1816	35.2	0.92	9609
25%W+FA	25% waste loaded with fly ash as filler	9.73	8.1	213	2.39	46.8	1796	36.3	0.91	9418
20%W+CaSi	20% waste loaded with calcium silicate as filler	4.28	5.9	187	2.24	45.5	74.2	18.9	0.81	8832
25%W+CaSi	25% waste loaded with calcium silicate as filler	5.31	9.2	230	3	56.2	100	23.9	1.21	11763

Table 7-5. TCLP results on various waste forms (mg/L)

	As	Se	Cr	Ag	Cd	Ba	Pb	Hg
20%W + FA	0.103	0.078	0.072	0.002	0.027	0.027	0.005	<0.0007
25%W+FA	0.091	0.107	0.114	0.002	0.006	0.012	0.005	<0.0007
20%W + CaSi	0.054	0.015	0.02	0.002	0.002	0.008	0.005	<0.0007
25%W + CaSi	0.091	0.026	0.02	0.002	0.016	0.134	0.005	<0.0007
Universal Treatment Standard (UTS)	5	5.7	0.6	0.14	0.11	21	0.75	0.025

7.2 Summary

Containment of RCRA metals does not appear to be an issue at the waste stream loading levels studied. It is quite possible that the waste streams with higher RCRA metal concentrations could be stabilized, or efficient waste forms with high waste loading can be produced.

8 CONCLUSIONS

The Ceramicrete process has been demonstrated to stabilize nitric acid waste simulant that is generated at the CNS Y-12 complex. Based on the recipes provided by CNS, a waste simulant was prepared in-house. The waste forms were fabricated with two filler materials: Class C fly ash and CaSiO_3 . For the fly ash and CaSiO_3 , waste loadings were as high as 25 wt.%.

The samples were subjected to physical property characterizations, ANS 16.1 leach tests, and TCLP tests. For the physical property characterizations, the waste forms were fabricated with a radionuclide surrogate, cerium, but did not have any hazardous contaminants. For the ANS 16.1 test samples, the waste simulants contained appropriate amounts of cerium and RCRA metals. The TCLP waste forms contained the requisite amounts of hazardous metals.

The physical property characterizations (density, compressive strength, and 90-day water immersion) showed that the waste forms are stable and durable. Compressive strengths were $>2,000$ psi, and these strengths were retained after 90-day water immersions test for the three waste simulants. The waste form weight loss was $\sim 2\text{-}3$ wt.%, which occurred during the initial part of the immersion test, indicative of washing-off of residual unreacted powder. The compressive strength measured after the immersion tests did not show any drop in the strength values; on the contrary, there was some increase in the compressive strengths. This behavior is believed to be due to curing of the binder phase during the immersion testing.

The ANS 16.1 tests yielded a leachability index for Ce of ~ 30 for all the samples evaluated. Further, binder phase elements such as Mg, Si, and Ca were >17 , indicating that the waste forms are highly insoluble. The RCRA elements were analyzed in the ANS 16.1 leachates, and the determined leachability indices were significantly higher than the acceptable value of 6. Further, no discernible degradation of the waste forms was apparent in the samples after the ANS 16.1 tests.

The TCLP results showed that all the hazardous contaminants are contained, and their concentrations are below the UTS limits.

9 RECOMMENDATIONS

Based on the results and observations from this study, we concluded that the Ceramicrete technology has the potential to stabilize and contain the nitric acid waste effluent at the CNS Y-12 complex. Waste loadings as high as 25 wt.% can be attained. In terms of filler materials, Class C fly ash and CaSiO_3 are adequate. However, CaSiO_3 appears to have relatively better structural integrity.

Although the present study was focused up to 25 wt.% waste loading, it is quite possible that waste loadings could be further increased. This needs to be established.

The compressive strengths measured after the water immersion tests appeared to increase, especially for the CaSiO_3 filler. This observation needs to be further examined to optimize the waste form in terms of waste loadings and other factors.

The leachability indices of Ce need to be improved to meet or exceed the target value of 6 for all the waste forms. As mentioned earlier, use of cerium oxide as the source of cerium in the waste simulant may not be ideal, since it is insoluble. In this regard, soluble cerium sulfate is a better option. Samples fabricated using cerium sulfate need to be evaluated for leaching tests.

Finally, bench-scale waste forms can be fabricated. For scaleup of the process, the binder phase, temperature rise, uniformity of the waste form, working time, etc., need to be optimized with respect to the final waste form performance.

REFERENCES

1. D. Singh, A. S. Wagh, J. C. Cunnane, and J. L. Mayberry, "Chemically Bonded Phosphate Ceramics for Low-Level Mixed-Waste Stabilization," *J. Environ. Sci. Health*, A32(2): 527-541 (1997).
2. A. S. Wagh, S.-Y. Jeong, and D. Singh, "High Strength of Phosphate Cements Using Industrial Byproduct Ashes," *Proc. of Conference on High Strength Cements*, Hawaii (1999).
3. D. Singh, V. R. Mandalika, S. J. Parulekar, and A. S. Wagh, "Magnesium Potassium Phosphate Ceramic for ^{99}Tc Immobilization," *J. Nuclear Materials* 348: 272-282 (2006).
4. A. S. Wagh, R. Strain, S.-Y. Jeong, D. Reed, T. Krause, and D. Singh, "Stabilization of Rocky Flats Pu-contaminated Ash Within Chemically Bonded Phosphate Ceramics," *J. Nuclear Materials* 265:295-307 (1999).
5. A. S. Wagh, D. Singh, and S.-Y. Jeong, "Chemically Bonded Phosphate Ceramics for Stabilization and Solidification of Mixed Wastes," in *Hazardous and Radioactive Waste Treatment Technologies Handbook*, ed., C. H. Ho, CRC Press, New York (2001).
6. Environmental Protection Agency, "Test Method 1311: Toxicity Characteristic Leaching Procedure," <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf>.
7. American Nuclear Society, "American National Standard Measurement of the Leachability in Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure," Method ANSI/ANS 16.1-1986, American Nuclear Society, La Grange Park, IL (1986).
8. Nuclear Regulatory Commission, "Nuclear Regulatory Commission Branch Technical Position on Waste Forms," Washington D.C. (1991).

APPENDIX A: COMPRESSIVE STRENGTH DATA

A.1 As-fabricated Waste Forms

Sample type	Compressive Strength (lb/in. ²)	Standard deviation (lb/in. ²)
15W-FA	2054	607
20W-FA	2202	311
25W-FA	878	299
15W-CaSi	4795	132
20W-CaSi	4239	465
25W-CaSi	3594	263

A.2 Post Water Immersion Test

Immersion Time	15W-FA (psi)	20W-FA (psi)	25W-FA (psi)	St. Dev. (15W-FA) (psi)	St. Dev. (20W-FA) (psi)	St. Dev. (25W-FA) (psi)
As fabricated	2238	2770	1044	401	358	357
1 month	3725	3389	1044	491	922	279
2 months		2045	1552		174	314
3 months	2920	2878	2370	236	891	640

Immersion Time	15W-CaSi (psi)	20W-CaSi (psi)	25W-CaSi (psi)	St. Dev. (15W-CaSi) (psi)	St. Dev. (20W-CaSi) (psi)	St. Dev. (25W-CaSi) (psi)
As fabricated	4796	4239	3595	132	465	263
1 month	4337	4740	3592	435	494	140
3 months	4328	4804	3570	285	865	638

APPENDIX B: AVERAGE WEIGHT LOSS DATA

Results based on average of three samples. Average initial sample weights were ~25-30 g.

Time (days)	15W-FA		20W-FA		25W-FA	
	ΔW (g)	St. Dev. (g)	ΔW (g)	St. Dev. (g)	ΔW (g)	St. Dev. (g)
0	0.000	0.000	0.000	0.000	0.000	0.000
10	0.350	0.052	0.310	0.062	1.330	0.050
20	0.580	0.043	0.530	0.093	1.800	0.229
30	0.590	0.040	0.540	0.112	1.970	0.238
60	0.380	0.025	0.310	0.189	1.750	0.145
90	0.400	0.020	0.370	0.220	1.780	0.110

Time (days)	15W-CaSi		20W-CaSi		25W-CaSi	
	ΔW (g)	St. Dev. (g)	ΔW (g)	St. Dev. (g)	ΔW (g)	St. Dev. (g)
0	0.000	0.000	0.000	0.000	0.000	0.000
10	0.990	0.041	0.830	0.061	1.330	0.052
20	1.220	0.055	1.130	0.074	1.710	0.043
30	1.320	0.074	1.280	0.077	1.880	0.071
60	2.200	0.178	1.980	0.134	3.000	0.235
90	2.560	0.040	2.540	0.140	3.210	0.460

APPENDIX C: DIFFUSIVITIES OF SELECTED CERAMICRETE WASTE FORMS AS OBTAINED FROM ANS 16.1 TEST

20W-FA-H1					
Δt (hours)	t (hours)	D_P (cm ² /s)	D_{Si} (cm ² /s)	D_{Ce} (cm ² /s)	D_{Mg} (cm ² /s)
2	2	2.56E-20	2.3E-15	5.69E-13	1.3E-20
5	7	2.1E-19	1.42E-14	1.09E-12	1.71E-20
17	24	2.45E-20	6.7E-14	7.8E-13	5.12E-21
24	48	3.16E-20	1.21E-13	1.42E-12	6.31E-21
24	72	1.6E-19	1.68E-13	3.25E-12	1.07E-20
24	96	3.39E-19	2.07E-13	5.92E-12	1.51E-20
24	120	8.36E-20	2.44E-13	8.13E-12	1.94E-20
336	456	4.73E-22	9.24E-14	4.08E-13	2.4E-22
672	1128	3.42E-22	6.39E-14	6.57E-13	1.74E-22
20W-FA-H2					
Δt (hours)	t (hours)	D_P (cm ² /s)	D_{Si} (cm ² /s)	D_{Ce} (cm ² /s)	D_{Mg} (cm ² /s)
2	2	9.26E-20	5.23E-13	5.23E-13	1.42E-20
5	7	1.28E-19	9.13E-13	9.13E-13	1.87E-20
17	24	1.1E-20	3.94E-13	3.94E-13	5.6E-21
24	48	1.36E-20	4.38E-13	4.38E-13	6.9E-21
24	72	1.18E-19	8.68E-13	8.68E-13	1.17E-20
24	96	2.06E-19	1.68E-12	1.68E-12	1.65E-20
24	120	5.64E-20	2.51E-12	2.51E-12	2.12E-20
336	456	5.17E-22	6.97E-14	6.97E-14	2.63E-22
672	1128	1.67E-21	2.04E-13	2.04E-13	1.9E-22

25W-FA-H1					
Δt (hours)	t (hours)	D_p (cm ² /s)	D_{Si} (cm ² /s)	D_{Ce} (cm ² /s)	D_{Mg} (cm ² /s)
2	2	9.67E-20	5.52E-13	5.52E-13	1.46E-20
5	7	1.35E-19	9.64E-13	9.64E-13	1.93E-20
17	24	1.18E-20	4.16E-13	4.16E-13	5.76E-21
24	48	1.45E-20	4.63E-13	4.63E-13	7.1E-21
24	72	1.25E-19	9.16E-13	9.16E-13	1.21E-20
24	96	2.16E-19	1.77E-12	1.77E-12	1.7E-20
24	120	5.9E-20	2.65E-12	2.65E-12	2.19E-20
336	456	5.52E-22	7.36E-14	7.36E-14	2.7E-22
672	1128	1.76E-21	2.16E-13	2.16E-13	1.95E-22
25W-FA-H2					
Δt (hours)	t (hours)	D_p (cm ² /s)	D_{Si} (cm ² /s)	D_{Ce} (cm ² /s)	D_{Mg} (cm ² /s)
2	2	4.42E-18	2.9E-15	1.08E-12	1.6E-20
5	7	4.87E-20	2.35E-14	3.6E-12	2.11E-20
17	24	1.27E-20	1.07E-13	1.27E-12	6.29E-21
24	48	1.57E-20	2.72E-13	1.37E-12	7.75E-21
24	72	6.37E-20	3.83E-13	2.58E-12	1.32E-20
24	96	3.74E-20	4.9E-13	4.66E-12	1.85E-20
24	120	1.49E-19	5.83E-13	6.61E-12	2.39E-20
336	456	5.96E-22	2.5E-13	2.61E-13	2.95E-22
672	1128	4.31E-22	1.62E-13	1.57E-12	2.13E-22

20W-CaSi-H1						
Δt (hours)	t (hours)	D_P (cm ² /s)	D_{Si} (cm ² /s)	D_{Ca} (cm ² /s)	D_{Ce} (cm ² /s)	D_{Mg} (cm ² /s)
2	2	1.32E-18	1.96E-13	1.34E-14	3.91E-21	1.4E-18
5	7	3.29E-19	9.53E-13	1.51E-14	5.16E-21	1.79E-19
17	24	6.31E-20	5.36E-12	1.44E-14	1.54E-21	3.37E-20
24	48	2.45E-20	7.49E-12	1.39E-14	1.9E-21	6.5E-21
24	72	6.89E-20	5.99E-12	2.55E-14	3.23E-21	8.14E-21
24	96	2.09E-20	4.75E-12	4.83E-14	4.54E-21	1.39E-21
24	120	1.44E-19	3.42E-12	4.45E-14	5.85E-21	6.12E-21
336	456	6.38E-21	4.67E-12	2.84E-15	7.24E-23	3.68E-21
672	1128	2.41E-22	4.76E-12	3.86E-15	5.23E-23	9.1E-23
20W-CaSi-H2						
Δt (hours)	t (hours)	D_P (cm ² /s)	D_{Si} (cm ² /s)	D_{Ca} (cm ² /s)	D_{Ce} (cm ² /s)	D_{Mg} (cm ² /s)
2	2	1.09E-18	1.6E-13	8.97E-15	4.02E-21	1.06E-18
5	7	3.3E-19	1.06E-12	1.65E-14	5.3E-21	1.65E-19
17	24	4.24E-20	4.86E-12	1.44E-14	1.58E-21	2.09E-20
24	48	1.15E-20	7.26E-12	1.7E-14	1.95E-21	2.83E-21
24	72	7.28E-20	5.07E-12	3.85E-14	3.31E-21	7.93E-21
24	96	8.38E-20	3.65E-12	3.41E-14	4.66E-21	5.13E-21
24	120	1.44E-19	2.46E-12	4.8E-14	6.01E-21	5.64E-21
336	456	3.42E-22	3.64E-12	4.15E-15	7.43E-23	1.82E-22
672	1128	2.47E-22	3.81E-12	6.22E-15	5.37E-23	8.61E-23

25W-Casi-H1						
Δt (hours)	t (hours)	D_P (cm ² /s)	D_{Si} (cm ² /s)	D_{Ca} (cm ² /s)	D_{Ce} (cm ² /s)	D_{Mg} (cm ² /s)
2	2	6.68E-19	3.5E-13	9.45E-15	4.01E-21	6.86E-19
5	7	2.16E-19	2.05E-12	1.62E-14	5.29E-21	1.13E-19
17	24	1.68E-20	5.88E-12	1.13E-14	1.58E-21	8.65E-21
24	48	9.2E-21	1.51E-11	2.49E-14	1.95E-21	2.36E-21
24	72	1.56E-20	2E-11	2.04E-14	3.31E-21	1.78E-21
24	96	2.2E-20	1.95E-11	1.96E-14	4.65E-21	1.41E-21
24	120	3.59E-20	1.71E-11	2.94E-14	5.99E-21	1.47E-21
336	456	3.5E-22	1.04E-11	1.91E-15	7.41E-23	1.95E-22
672	1128	6.17E-21	6.9E-12	6.77E-15	5.36E-23	2.25E-21
25W-Casi-H2						
Δt (hours)	t (hours)	D_P (cm ² /s)	D_{Si} (cm ² /s)	D_{Ca} (cm ² /s)	D_{Ce} (cm ² /s)	D_{Mg} (cm ² /s)
2	2	1.56E-19	3.3E-13	7.56E-15	4.02E-21	1.62E-19
5	7	9.49E-19	1.68E-12	1.12E-14	5.3E-21	5.02E-19
17	24	3.72E-20	5.58E-12	1.28E-14	1.58E-21	1.94E-20
24	48	8.99E-21	1.31E-11	1.31E-14	1.95E-21	2.33E-21
24	72	7.24E-20	1.71E-11	2.75E-14	3.31E-21	8.34E-21
24	96	1.3E-19	1.44E-11	2.52E-14	4.66E-21	8.44E-21
24	120	1.41E-19	1.21E-11	3.17E-14	6.01E-21	5.83E-21
336	456	3.42E-22	1.06E-11	2.5E-15	7.43E-23	1.93E-22
672	1128	2.47E-22	7.83E-12	3.28E-15	5.37E-23	9.11E-23

APPENDIX D: TCLP DATA

20W-FA

GEL Laboratories LLC

METALS
-1-
INORGANICS ANALYSIS DATA PACKAGE

SDG No: 398599

METHOD TYPE: SW846

SAMPLE ID: 398599001

CLIENT ID: 20W-FA-H

CONTRACT: ARGN006LCS

MATRIX: TCLP

DATE RECEIVED 03-JUN-16

LEVEL: Low

<u>CAS No</u>	<u>Analyte</u>	<u>Result</u>	<u>Units</u>	<u>C</u>	<u>Qual</u>	<u>M*</u>	<u>MDL</u>	<u>DF</u>	<u>Inst ID</u>	<u>Analytical Run</u>
7440-38-2	Arsenic	0.103	mg/L			MS	0.017	1	ICPMS12	160616-2
7440-39-3	Barium	0.0273	mg/L			MS	0.006	1	ICPMS12	160615-1
7440-43-9	Cadmium	0.0274	mg/L			MS	0.0011	1	ICPMS12	160615-1
7440-47-3	Chromium	0.0718	mg/L	B		MS	0.02	1	ICPMS12	160615-1
7439-92-1	Lead	0.005	mg/L	U		MS	0.005	1	ICPMS12	160615-1
7439-97-6	Mercury	0.00067	mg/L	U		AV	0.00067	1	HG4	060816W1-3
7782-49-2	Selenium	0.0783	mg/L			MS	0.015	1	ICPMS12	160615-1
7440-22-4	Silver	0.002	mg/L	U		MS	0.002	1	ICPMS12	160615-1

*Analytical Methods:

MS SW846 3010A/6020A

AV SW846 7470A

25W-FA

GEL Laboratories LLC

METALS
-1-
INORGANICS ANALYSIS DATA PACKAGE

SDG No: 398599

METHOD TYPE: SW846

SAMPLE ID: 398599002

CLIENT ID: 25W-FA-H

CONTRACT: ARGN006LCS

MATRIX: TCLP

DATE RECEIVED 03-JUN-16

LEVEL: Low

<u>CAS No</u>	<u>Analyte</u>	<u>Result</u>	<u>Units</u>	<u>C</u>	<u>Qual</u>	<u>M*</u>	<u>MDL</u>	<u>DF</u>	<u>Inst ID</u>	<u>Analytical Run</u>
7440-38-2	Arsenic	0.0906	mg/L			MS	0.017	1	ICPMS12	160616-2
7440-39-3	Barium	0.0117	mg/L	B		MS	0.006	1	ICPMS12	160615-1
7440-43-9	Cadmium	0.0057	mg/L	B		MS	0.0011	1	ICPMS12	160615-1
7440-47-3	Chromium	0.114	mg/L			MS	0.02	1	ICPMS12	160615-1
7439-92-1	Lead	0.005	mg/L	U		MS	0.005	1	ICPMS12	160615-1
7439-97-6	Mercury	0.00067	mg/L	U		AV	0.00067	1	HG4	060816W1-3
7782-49-2	Selenium	0.107	mg/L			MS	0.015	1	ICPMS12	160615-1
7440-22-4	Silver	0.002	mg/L	U		MS	0.002	1	ICPMS12	160615-1

***Analytical Methods:**

MS SW846 3010A/6020A

AV SW846 7470A

20W-CaSi

GEL Laboratories LLC

METALS
-1-
INORGANICS ANALYSIS DATA PACKAGE

SDG No: 398599

METHOD TYPE: SW846

SAMPLE ID: 398599003

CLIENT ID: 20W-Casi-H

CONTRACT: ARGN006LCS

MATRIX:TCLP

DATE RECEIVED 03-JUN-16

LEVEL: Low

<u>CAS No</u>	<u>Analyte</u>	<u>Result</u>	<u>Units</u>	<u>C</u>	<u>Qual</u>	<u>M*</u>	<u>MDL</u>	<u>DF</u>	<u>Inst ID</u>	<u>Analytical Run</u>
7440-38-2	Arsenic	0.0543	mg/L			MS	0.017	1	ICPMS12	160616-2
7440-39-3	Barium	0.00778	mg/L	B		MS	0.006	1	ICPMS12	160615-1
7440-43-9	Cadmium	0.00161	mg/L	B		MS	0.0011	1	ICPMS12	160615-1
7440-47-3	Chromium	0.02	mg/L	U		MS	0.02	1	ICPMS12	160615-1
7439-92-1	Lead	0.005	mg/L	U		MS	0.005	1	ICPMS12	160615-1
7439-97-6	Mercury	0.00067	mg/L	U		AV	0.00067	1	HG4	060816W1-3
7782-49-2	Selenium	0.015	mg/L	U		MS	0.015	1	ICPMS12	160615-1
7440-22-4	Silver	0.002	mg/L	U		MS	0.002	1	ICPMS12	160615-1

***Analytical Methods:**

MS SW846 3010A/6020A
AV SW846 7470A

25W-CaSi

GEL Laboratories LLC

METALS
-1-
INORGANICS ANALYSIS DATA PACKAGE

SDG No: 398599

METHOD TYPE: SW846

SAMPLE ID: 398599004

CLIENT ID: 25W-Casi-H

CONTRACT: ARGN006LCS

MATRIX:TCLP

DATE RECEIVED 03-JUN-16

LEVEL: Low

<u>CAS No</u>	<u>Analyte</u>	<u>Result</u>	<u>Units</u>	<u>C</u>	<u>Qual</u>	<u>M*</u>	<u>MDL</u>	<u>DF</u>	<u>Inst ID</u>	<u>Analytical Run</u>
7440-38-2	Arsenic	0.0905	mg/L			MS	0.017	1	ICPMS12	160616-2
7440-39-3	Barium	0.134	mg/L			MS	0.006	1	ICPMS12	160615-1
7440-43-9	Cadmium	0.0166	mg/L			MS	0.0011	1	ICPMS12	160615-1
7440-47-3	Chromium	0.02	mg/L	U		MS	0.02	1	ICPMS12	160615-1
7439-92-1	Lead	0.005	mg/L	U		MS	0.005	1	ICPMS12	160615-1
7439-97-6	Mercury	0.00067	mg/L	U		AV	0.00067	1	HG4	060816W1-3
7782-49-2	Selenium	0.0262	mg/L	B		MS	0.015	1	ICPMS12	160615-1
7440-22-4	Silver	0.002	mg/L	U		MS	0.002	1	ICPMS12	160615-1

***Analytical Methods:**

MS SW846 3010A/6020A
AV SW846 7470A

(Blank Page)



Energy Systems Division

Argonne National Laboratory
9700 South Cass Avenue, Bldg. 362
Argonne, IL 60439-4854

www.anl.gov



Argonne National Laboratory is a U.S. Department of Energy
laboratory managed by UChicago Argonne, LLC